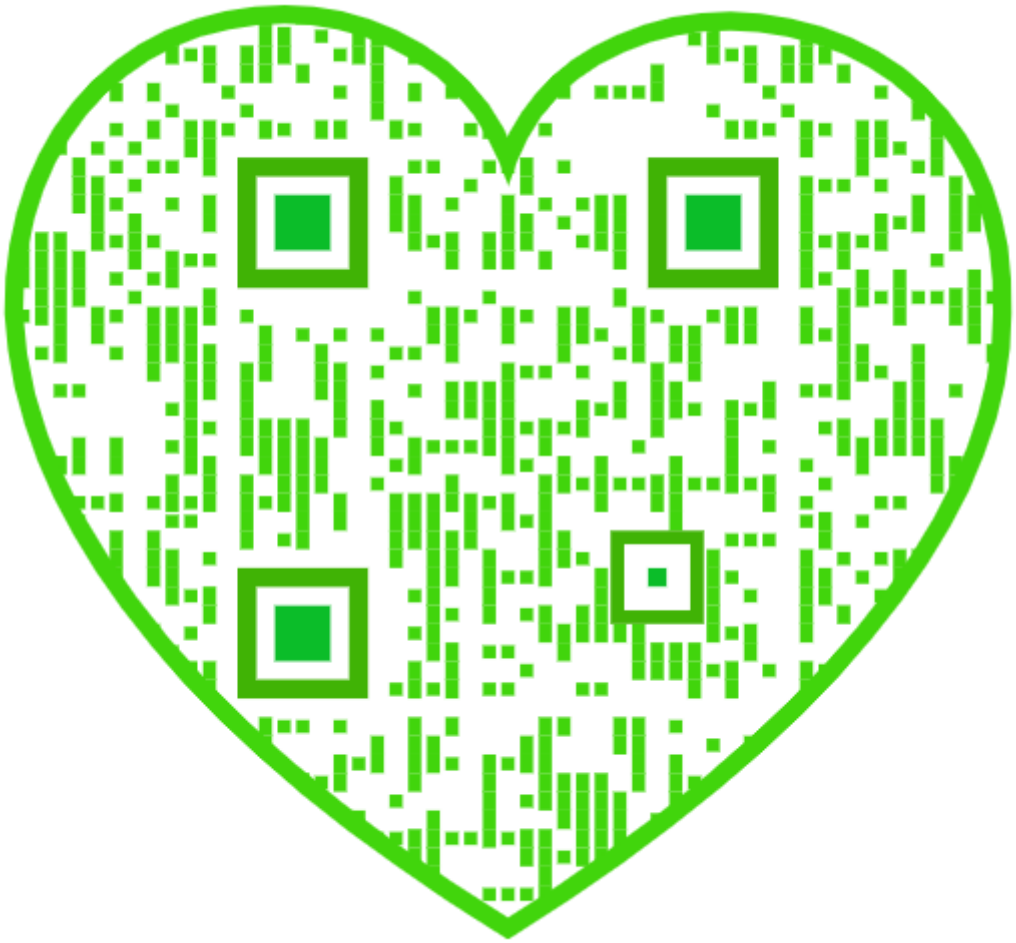

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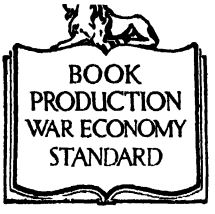

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EDITORIAL PREFACE

In these days of intensive and extensive research, every worker in science or its applications knows how rapidly the contents of text-books and encyclopædias become out of date ; and those who wish to see new work published know the difficulties which abnormal taxation and high labour costs offer to the realisation of their desire. The one obvious solution of the problem is the publication of monographs that would focus attention upon recent work, or upon new aspects of old work, and upon their theoretical implications. Such books are usually written by experts for other experts in related fields of science, or for the well-educated layman whose thirst for new knowledge has not been quenched by the more sensuous outpourings of the ephemeral press.

It is interesting at times to speculate upon what aspects of our civilisation the future historian will select as the most characteristic of our time. Scientific discoveries and their application to human welfare, we may be sure, will find a place ; and to these many will add the growth of our sense of " values." The value of new work in science varies greatly : the golden grain is always accompanied by chaff, and there is no precious ore without country rock. Owing to the difficulty of assessing the value of work at the time of its production, we find that our scientific periodicals stand in danger of being swamped by the mass of second- and third-rate material that is thought to be worth publishing, but which posterity will decree would have been better left in manuscript form. It is the first duty of the monograph writer to estimate the value, either actual or potential, of recent work upon the subject of which he writes : he must pick out the plums to save others from the indigestion that follows eating the whole pie. Further, in addition to being accurate, his work must be presented in a form that is both assimilable and attractive ; in other words, he must show that lucid exposition can be achieved by the use of few words, if they are rightly chosen, and that attractive presentation is attained rather by clear thinking than by superficial display.

The present series of monographs has been designed with these objects and ideals in view. The task which the authors have been set is no easy one ; so that should performance occasionally fall short of intention, the critical reader is asked to echo the words of Goethe that " higher aims, even if unfulfilled, are in themselves more valuable than lower aims quite attained."

E. Howard Tripp.

PREFACE TO THE FIRST EDITION

BOTH the number of organic solvents which are available to industry and the extent to which they are used have increased greatly during recent years, and there is in consequence a need for a scientific exposition of the technical application of solvents, more particularly in connection with the cellulose-lacquer industry.

A vast mass of valuable information germane to the subject is scattered widely throughout scientific and technical literature, but it is often presented in a profuse manner, lacking cohesion and clarity.

The author has attempted to bring this information into a concise form wherein the scientific and fundamental aspects of the subject are expressed in a readily comprehensible manner, and to show the relations of these aspects to technical usage.

The first part of this book takes the form of a more or less connected series of chapters dealing with the scientific fundamentals in a broad and simple manner. The second part is of a more utilitarian nature and deals comprehensively with individual solvents, mainly with the view of facilitating the intelligent use of these solvents in the cellulose-lacquer industry.

This book is not designed to deal with the actual manufacture of lacquers or varnishes, this aspect being the subject of a book in this series by another author.

I have to express my thanks to the Directors of Messrs. A. Boake, Roberts & Co., Ltd., for the facilities they have afforded me in the compilation of this book. I have also to thank M. F. Carroll, Esq., M.Sc., and F. H. Mackenzie, Esq., for their kindness in reading and correcting my manuscript.

T. H. D.

PREFACE TO THE SECOND EDITION

THE present edition has been thoroughly revised and much additional information has been included. Particular attention is drawn to the chapters on Plasticising Solvents, which have been considerably extended.

In response to requests from several quarters there has

been added as an appendix a comprehensive table of solubilities in which ethyl cellulose has been included and also a complete dictionary of trade names.

Details are also included of certain new solvents which have made their début during the brief interval between the first and second editions. More attention has been paid to the many azeotropic mixtures which are known to occur among commonly used solvents, as these deserve more attention than hitherto paid to them ; their practical significance is also discussed

I should like to express my thanks to my colleague A. L. Bloomfield, Esq., B.A., B.Sc., for many valuable suggestions.

T. H. D.

PREFACE TO THE THIRD EDITION

THE great activity and constant advance shown by the lacquer and similar industries necessitates the continual revision and amplification of any collection of information regarding solvents. No apology is therefore offered for publishing three separate editions of this book in the course of a little over three years.

While no deep-seated advance has been made in the science of the subject since the publication of the second edition, technically there is much which is new and cannot be ignored. A number of new solvents and plasticisers are now available industrially and have widened the field of possible technical applications considerably.

The endeavour has been made to make this third edition as comprehensive as feasible, and with this in view, information has been included regarding certain new solvents which, while not available technically, are potentially of great interest. There has also been added a plasticiser-dosage table, which it is felt may be of some practical value, while the list of trade names has been considerably amplified.

The author desires to acknowledge gratefully the valuable criticisms offered by Dr. Otto Merz, the translator of the German Edition.

T. H. D.

PREFACE TO THE FOURTH EDITION

In the period which has elapsed since the third edition of this book was issued in 1933, considerable advances have been made in the production of solvents and plasticisers and in the elucidation of the scientific principles involved in their use. The necessity for a complete revision and amplification of the book has therefore arisen, at the same time the author has endeavoured to make the book of use to a somewhat wider industrial field, as has been shown to be desirable, without overloading the text by the inclusion of matter of doubtful utility.

Particular attention is called to the section dealing with plasticising solvents and toxicity, which have been rewritten ; to the enlargement of the appendices and to the inclusion in an abridged form of the latest specifications issued by the British Standards Institution and by the American Society for Testing Materials ; the author desires to thank these authorities for the facilities accorded to him.

T. H. D.

PREFACE TO THE FIFTH EDITION

The main scope and general form of the fifth edition of this book remains as originally conceived but, as in previous editions, much additional detail has been included in order to widen its utility. The opportunity has been taken to eliminate obsolescent material and generally to check accuracy. As is to be expected the war has dislocated the Solvent Industry, but it has been thought best, in the main, to disregard those effects which appear to be transient.

The section dealing with petroleum hydrocarbons has been rewritten and my grateful thanks are due to C. L. Gilbert, Esq., and other gentlemen of the Asiatic Petroleum Co., Ltd., for their assistance.

T. H. D.

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PART I

INTRODUCTION

A SOLVENT may be defined as a substance by means of which a solid may be brought to a fluid state. This definition, although defective and inadequate, expresses the general idea underlying the use of solvents. In the case of " cellulose lacquers " the object of employing a solvent is merely to provide a means of transferring a solid—cellulose ester—from one place to another in a convenient and desirable manner ; when the transference has been accomplished the solvent is of no further use and has to be removed as rapidly and as completely as possible, but in a manner compatible with concomitant factors. These factors make it desirable that certain characteristics of a solvent should be known and that a solvent suitable for the purpose should be used.

The most important characteristics to be considered are :—

1. Solvent power.
2. Volatility.
3. Stability.
4. Toxicity.
5. Inflammability.
6. Colour.

These characteristics are not simple phenomena, but are each composed of several factors. One and the same factor may influence more than one of the characteristics ; thus, for instance, the vapour pressure of a solvent, which is largely governed by its molecular weight, affects its volatility, toxicity and inflammability ; and it is thought also to be related to its solvent power and the viscosity of its solutions.

In order the better to visualise the phenomena involved in the preparation and the use of lacquers it is desirable to examine the foundations underlying them, together with their practical significance.

CHAPTER I

SOLVENT ACTION

THE manner in which a solvent acts and the reason for its solvent action have been extensively investigated for many years, the first serious attempt to elucidate the *modus operandi* of solvents on colloids of the type of cellulose nitrate being that of F. Baker in 1912.[1]

It is well known that certain varieties of cellulose nitrate are soluble in a mixture of alcohol and ether, although not soluble in either liquid separately. Neither of these liquids contains any group, such as carbonyl, which usually imparts solvent properties, as, for instance, in acetone or amyl acetate.

As a result of his investigations Baker concluded that mixtures of ether and alcohol contain a molecular ether-alcohol complex to which the solvent properties of the mixture are due. The increase of solvent power with diminishing temperature * was ascribed to an increase in the proportion of this ether-alcohol complex.[2] A further conclusion [3] was that cellulose nitrate in solution is associated with the solvent, the true solute being not simply cellulose nitrate but a complex of it and the solvent.

In general, liquids which possess the highest solvent powers yield solutions of the lowest viscosity, and the fluidity of a solution is a measure of the solvent power of the solvent. Thus, in Baker's view, the viscosity of a solution depends on the nature of the complex solvent-cellulose nitrate, and in a homologous series of solvents, such as the acetic esters of the saturated aliphatic alcohols, the increase in viscosity corresponds with the increase in the molecular weight of the solvent.

The viscosity of a solution of cellulose nitrate in mixtures of ether and alcohol is dependent on the ratio of ether to alcohol and reaches a minimum at a definite ratio.[4] This ratio is a characteristic property of the particular cellulose nitrate, but it does not depend on the amount of it in the solution. The higher the nitrogen content of the cellulose nitrate, the greater is the proportion of ether required to obtain the solution of lowest viscosity.

* This is only true within limits.

If a solution of cellulose nitrate or acetate be cooled sufficiently a cloud develops. Assuming that the lower the temperature at which the cloud develops, the higher the solvent power of the solvent, Mardles [5] concluded that the solubility depends on the specific character of both the solvent and the cellulose ester (*cf.* p. 11).

When solvents are mixed there is usually a large divergence in solvent power from the average of the values ; many non-solvents becoming solvents on being mixed, whilst in some cases solvents on mixing lose their solvent properties.[9] The solvent behaviour of mixed liquids which are known to form, or are suspected of forming, molecular complexes, cannot be ascribed to the intrinsic action of one kind of molecule or molecular complex, and, in general, whenever molecular simplification occurs in a liquid mixture there is increased solvent action. Liquids having small molecules are the better dispersing media and give solutions of low viscosity ; and with rise of molecular weight there is a rapid decrease in solvent power. Any change which tends to increase molecular complexity causes a decrease in solvent action, and therefore, Mardles concludes, when compound formation occurs between the compounds of a binary mixture loss of solvent power results, he further concludes that in cases where mixtures containing molecular complexes are good solvents, such as in ether-alcohol mixtures, the effect of the complex formation is masked by that due to molecular dissociation, and hence, simplification of the liquids.

Byron [6] found that cellulose nitrate is peptised (*i.e.*, dissolved) by absolute alcohol at a low temperature owing to the adsorption of polymerised (associated) alcohol ; such a mixture on warming becomes viscous and sets to a jelly. Adsorption decreases, in general, with rising temperature, and it is known that associated liquids similarly tend to become simplified. Anhydrous ether does not peptise cellulose nitrate at any temperature, and it is suggested that the function of the ether in ether-alcohol solutions of cellulose nitrate is to cause the alcohol to polymerise, and thus to render it a peptising agent for cellulose nitrate.

Highfield [7] considers that cellulose nitrate contains both strongly polar (hydroxyl) and weakly polar (hydrocarbon) groups, and that the best solvents for it contain these two classes of groups in suitable proportions. This would

account for the better solvent action of certain solvent mixtures. The best composition of a solvent mixture, for instance of ether, alcohol and water, depends on the nitrogen content of the cellulose nitrate ; as this decreases the hydroxyl content increases and thus necessitates a corresponding increase in the number of hydroxyl groups in the solvent mixture, *e.g.*, alcohol.

Drummond[8] classifies solvents as polar and non-polar. The former class comprises solvents like alcohol and acetone which contain hydroxyl or carbonyl groups associated with strong polarity ; the high dielectric constants of these solvents are evidence of such polarity. Benzene, petroleum, and carbon disulphide, characterised by low dielectric constants, are non-polar.

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[1] *J.C.S.*, 1912, p. 1409. *Cf. Z. Chem. Ind. Koll.*, 1912, p. 284. *J.C.S.*, 1930, p. 1653.
[2] *Z. ges. Schuess- u. Sprengstoff w.*, 1907, p. 381.
[3] *J.C.S.*, 1913, p. 1653.
[4] GIBSON and MCCALL. *Chem and Ind.*, 1920, p. 172T.
[5] *Ibid.*, 1923, p. 127T., 1924, p. 224. *Cf.* SCHÜTZENBERGER. *Compt. rend.*, 1869, **68**, p. 814.
[6] *J. Physical Chem.*, 1926, **30**, p. 1116.
[7] *Trans. Faraday Soc.*, 1926, Jan., **22**, p. 57
[8] *J. Inst. Rubber Ind.*, 1928, p. 44. *Cf.* HILDEBRAND, " Solubility," A.C.S. monograph, N.Y., 1924
[9] *Ind. Eng.*, 1940, p. 519.

CHAPTER II

SOLVENT POWER

IF to a solution of cellulose nitrate a miscible non-solvent be gradually added, a dilution is ultimately reached, at which the cellulose nitrate begins to be thrown out of solution either as a precipitate or a gel. The solution is said to " tolerate " the addition of this definite proportion of the diluent under the conditions of temperature and cellulose-nitrate content obtaining. It is common to regard tolerances or dilution ratios as a measure of the solvent power of a solvent.

The dilution ratio is profoundly influenced by several factors, the more important of which are : (1) The nature of the cellulose nitrate or acetate. (2) The ratio of the amount of cellulose ester to that of its solvent. (3) The nature of the solvent or solvent mixture. (4) The nature of the diluent. (5) Temperature.

An empirical method for obtaining a measure of the solvent power of a solvent has been devised by Mardles, Moses and Willstrop, who suggested the following conditions :

The heptane fraction of petroleum spirit is added gradually from a burette to 5 c.c. of a 5 per cent. weight-volume solution of a cellulose ester at 20° C. The volume of heptane required just to cause persistent turbidity after two or three minutes' shaking, divided by the volume of original solution, is the solvent power number or the dilution ratio.

In America, slightly different conditions are usually employed, and are regarded as " standard," viz. :

Two grams of " half-second " cellulose nitrate are dissolved in 20 c.c. of the solvent under test. The volume of diluent required to cause permanent incipient precipitation at 20° C., divided by the volume of the solvent, represents the dilution ratio.

The dilution ratio can be described as the ratio of non-solvent to solvent at which the mixture ceases to be a solvent for nitro-cellulose above a given concentration.

The diluent most commonly employed for the test is toluene, the figures obtained varying widely with the diluent ;

thus butyl alcohol can usually be added in considerably greater quantity than can toluene, the reverse being the case with petroleum hydrocarbon (*vide* Table, p. 6).

The dilution ratio is an empirical number and represents the maximum quantity of a particular diluent which can be added to a particular solution, it represents an extreme limit and may not be of very great importance technically when considered in conjunction with other factors, such as vapour pressure or evaporation rate, since, for instance, if the diluent have an evaporation rate slower than that of the solvent it is not feasible to employ proportions even approaching that of the dilution ratio. It has been pointed out [1] that, for a technically useful result to be obtained, it is necessary that the final concentration of the solution plus diluent when precipitation occurs, should be comparable with that usually obtaining in lacquers, that is to say, from 8 to 10 per cent. of cellulose nitrate. Thus to add, as is frequently done, two, three or four volumes of diluent to one volume of a 10 per cent. solution of cellulose nitrate yields a solution which, at the precipitation point, bears no resemblance to the usual type of lacquer employed technically.

The following table shows how the dilution ratio varies with the final concentration. At high dilution the precipitation point is indefinite. The table also shows that the greater the initial concentration of the cellulose nitrate the less the amount of diluent that can be added.

Cellulose Nitrate.	Butyl Acetate.	Toluene	Final percentage of Cellulose Nitrate.	Dilution Ratio.
gms.	c.c.	c.c		
1·0	20	75	1·06	3·75
2·0	20	71	2·20	3·55
3·0	20	67	3·45	3·35
4·0	20	63	4·82	3·15

Dilution Ratios

The figures quoted below are the averages of determinations published by the most reliable authorities and refer in general to the results obtained with ½ sec. cellulose nitrate treated by methods approximating to that described on p. 4.

Solvent.	Diluent.			
	Toluene.	Xylene.	Petroleum.	Butanol.
Acetone	4·5	3·9	0·6	7·0
n-Amyl acetate	2·2	2·2	1·4	7·3
iso-Amyl acetate	2·7	2·4	1·4	7·3
iso-Amyl lactate	4·2	—	2·5	—
n-Butyl acetate	2·7	2·7	1·5	8·2
sec-Butyl acetate	2·6	2·5	1·2	8·2
n-Butyl glycollate	8·2	—	2·2	—
n-Butyl lactate	5·0	4·9	2·0	—
n-Butyl proprionate	2·3	2·3	1·3	7·5
Butyl cellosolve	4·0	—	2·3	—
Butylene glycol diacetate	2·3	—	—	—
Cyclohexyl acetate	2·6	—	1·2	—
Diacetone alcohol	3·1	2·9	0·5	7·8
Di Amyl phthalate	2·3	—	2·0	20·0
Di Amyl tartrate	9·8	—	—	—
Di Butyl oxalate	2·6	—	—	—
Di Butyl phthalate	2·8	2·7	1·7	8·0
Di Butyl tartrate	10·6	7·7	1·4	15·0
Di Ethyl carbonate	0·9	0·7	0·4	6·2
Di Ethyl oxalate	3·5	—	0·7	—
Di Ethyl phthalate	3·2	—	0·7	—
Di Glyceryl tetra-acetate	0·9	—	—	—
Di Methyl phthalate	2·5	—	—	—
Ethyl acetate	3·4	3·3	1·0	8·4
Ethyl lactate	5·6	4·8	0·7	10·2
Cellosolve	5·0	4·7	1·0	6·9
Cellosolve acetate	2·5	2·5	1·0	7·5
sec-Hexyl acetate	1·6	1·8	0·8	—
Methyl acetate	3·0	—	0·9	—
Methyl alcohol	2·5	—	0·3	—
Methyl ethyl ketone	4·5	3·3	—	—
Mesityl oxide	4·4	4·1	1·0	9·2
n-Propyl acetate	3·0	2·0	1·2	—
iso-Propyl acetate	2·9	2·9	1·0	8·8
Triacetin	0·9	—	—	—
Tributyl citrate	4·9	—	—	—
Triethyl citrate	3·9	—	—	—
Tributyl phosphate	24·0	—	—	—
Tricresyl phosphate	3·3	4·2	0·7	4·9

The figures should be regarded as indicative rather than accurately quantitative.

Liquids which are solvents for both cellulose nitrate and

acetate generally have much higher dilution ratios with the former than with the latter, the nitrate solution being able to hold considerably more diluent; in both cases the nature of the diluent has a profound effect; indeed, quite frequently, two non-solvents, one of which is an alcohol, when mixed together give a powerful solvent mixture. A classical example is that of ether-alcohol mixture dissolving cellulose nitrate. The same phenomenon is exhibited in the case of glyceryl phthalate resins, the less highly polymerised forms of which are soluble in esters of the type of butyl acetate to which has been added an alcohol such as amyl alcohol or ethyl alcohol. Mixtures of toluene and ethyl alcohol dissolve these resins and also cellulose nitrate, whilst benzene-alcohol mixture dissolves cellulose nitrate of nitrogen content up to about 11 per cent. It is known that esters, such as ethyl acetate and butyl acetate, are better solvents for mixtures of cellulose nitrate and resins when the corresponding alcohol is present than when in a pure and completely esterified state. Thus 85 to 88 per cent. ethyl acetate has a dilution ratio of 3·5 for toluene while the purer 99 to 100 per cent. has one of 3·0. The addition of quite a small quantity of butyl or benzyl alcohol to a hazy lacquer will not infrequently clarify it. More often, however, the effect of using two non-solvents simultaneously is merely that of the cumulative effects of each non-solvent separately.

References

[1] BROWN and BOGIN. *Ind. Eng. Chem.*, 1927, p. 969.

CHAPTER III

PLASTICISING SOLVENTS

PLASTICISERS are substances of very low volatility which possess the power of increasing the flexibility of cellulose esters. Flexible bodies may be of two types, the elastic type which regains its shape after the removal of the deforming force, such as rubber, and the plastic type which does not regain its shape, such as putty. Actually all bodies have both properties, elasticity and plasticity, in varying degrees, and by the appropriate choice and application of a plasticiser, it is possible more or less to control these properties in cellulose ester films, which normally are brittle and cannot be greatly deformed without fracture.

Plasticisers have, in general, the effect of rendering cellulose esters less hard and more plastic. The plastic form has less tensile strength than the elastic, but by reason of its plasticity it is subject to less strain after deformation and is in consequence the more durable. A plasticised film yields to a force to a greater extent without fracture than will an unplasticised more elastic film, but the unplasticised film generally withstands the greater force ; in other words, the plasticised film has the greater extensibility. In practice it is necessary to effect a compromise between this increase of extensibility or plasticity and the accompanying softness of the surface or lack of rigidity.

If a solution of cellulose ester be allowed to evaporate so as to leave a film, there occurs firstly a relatively very rapid loss of solvent, the rate of loss depending, among other factors, on the vapour pressure of the solvent under the conditions which exist. This loss occurs initially, in the case of a solution made with a single solvent, at an almost constant rate until a viscosity is reached in the film which is such that the free movement of the particles of solvent to the surface of the film is restricted to a degree sufficient to retard evaporation of the solvent from the surface. At this point there follows either a rapid slowing up of the evaporation rate in the case of highly volatile solvents—*i.e.*, low boilers—or a long drawn

out retardation in the case of solvents of low volatility—*i.e.*, high boilers. The second period is that in which the so-called " secondary flow " occurs and to which the final gloss or smoothness of the surface is largely due. The third period, which is the one most concerned here and which critically affects the life of the film, is that in which the remaining solvent evaporates with extreme slowness, imparting an evanescent plasticity to the film. The loss of solvent which ensues during this third period in a more or less rigid unplasticised mass results in stresses caused by the inability of the mass to adjust its shape ; it is probable that the cracking which occurs with old celluloid film plasticised with the volatile substance camphor is due more to the loss of plasticity than to degradation of the cellulose nitrate. In an unplasticised or insufficiently plasticised film, traces of a relatively non-volatile solvent may persist for many years, but as time elapses the amount continuously diminishes, the film in consequence becomes progressively harder and more brittle, a state of true stability never being reached. The time necessary for the film to become brittle depends on the volatility of the solvent, the thickness of the film, the temperature, the degree of exposure and similar factors.

Of these factors, the only one that is initially under control is the volatility of the solvent, but this volatility has to conform with other requirements, such as the avoidance of " chilling " or " blushing," the ease of application of the lacquer, and the speed of drying and its consequent effect on " flow." It is obviously highly desirable to eliminate as far as possible the effect of the solvent on the ultimate nature of the film. To this end it is preferable to employ a solvent with as high a degree of volatility as is commensurate with the other requirements, in order to obtain quickly a film devoid of solvent. A film such as this would be highly brittle, and it is mainly for the purpose of avoiding or regulating this brittleness that plasticisers are used.

During the later stages of evaporation the size of the molecules of the solvent is the prime factor governing the rate of evaporation, since the larger the molecule the slower the diffusion to the surface. Hence the solvent which it is desired to eliminate from the film should have a small molecule, while for plasticisers, substances of high molecular weight are desirable, both for this reason and for the concomitant

phenomenon of low volatility: there is, however, a practical limit in the case of plasticisers beyond which no useful purpose is served and which arises in the manufacture of plasticisers. Further, with increasing molecular weight there is usually a diminution of the mutual solubility between the cellulose ester and the plasticiser. Thus many of the highly complex plasticisers of excessively high molecular weight have little or no solubility in cellulose esters and are similar in their action to the resins and castor oil.

With plastic masses in contradistinction to films, the conditions which apply are somewhat different. The volatile part of the solvent evaporates as freely if not more freely from the surface of the mass than from a film: we can regard the surface of a mass as a film which is receiving further supplies of volatile solvent from the interior. There is in effect a stabilisation of the surface and in consequence a higher rate of loss of solvent per given area of exposed surface can be tolerated in a mass than in a film. It is, therefore, not so essential to select solvents or plasticisers outside the 150°–250° boiling range and, indeed, the higher solvent powers of this class as compared with the plasticisers proper is of assistance where moulding under heat and pressure is concerned. With masses of considerable thickness the tendency should be to avoid the use of low boiling solvents and to rely not on loss of solvent to effect rigidity but on the adequate dispersion of the solvent in the cellulose ester. The use of a solvent plasticiser permits a plastic, which is solid at ordinary temperatures, to become on heating sufficiently soft and ductile to be pressed and moulded into desired shapes: with non-solvent softeners of the castor-oil type, the use of heat and pressure merely results in the expression of the oil without sufficient softening of the cellulose nitrate to permit moulding.

During the last few years there has been a tendency towards the use of resins as plasticisers for cellulose esters; resins may be considered as being of two types: the first, which has no solvent action on cellulose esters, may be regarded as the solid analogue of castor oil, which is merely held in the intercellular spaces in the cellulose ester, forming no "compound" therewith. Such resins give opaque mixtures, due to the existence of two solid phases, but these can be brought into a one-phase solution by the addition of a plasticiser which is a mutual solvent for both the resin and

cellulose ester, thus changing the hard, elastic but brittle mass into a more plastic and more transparent mass. The second type of resin, of which but few are known, is in itself a solvent for the cellulose ester. The addition of a plasticiser which is a solvent for the resin causes a lowering of the softening point: a resin which is itself a solvent for the cellulose ester requires no such addition and the softening point is in consequence not lowered. Resins which do not form solutions with cellulose nitrate lower the plasticity and increase the brittleness, while those which do form solutions increase durability and weather resistance may be used in large proportions.

The lines of demarcation between high boiling solvents, plasticisers and resins as regards volatility cannot be accurately defined; it can, however, be said that the volatility of the resins is so low that it may be ignored, but there is great difficulty in deciding where to draw the line between the other two. The volatility of a plasticiser in a film under actual conditions of exposure is for several reasons very difficult to measure: the issue has still further been obscured by the publication of many incredible results on the volatility of plasticisers in the free state: such results seem to be without value, firstly, because of the invalidity of the methods employed and, secondly, because they take no account of the influence of the cellulose esters and resins with which the plasticisers are commonly used.

Plasticisers also exercise the function of preventing or limiting to a large extent the retention of volatile solvent by films. Cellulose esters have the property of associating with a more or less definite amount of a solvent, forming a loosely bound complex from which the solvent evaporates much more slowly than it would if such association did not occur; with mixtures of solvents the less volatile is retained at the expense of the more volatile; plasticisers, being solvents of very low volatility, accordingly permit the low boiling solvents to leave the film with greater ease than in the absence of a plasticiser.

Resins which are not, in the absence of a common solvent, compatible with cellulose esters do not perform this function, but a resin which is itself a plasticiser for cellulose esters will prevent the protracted retention of volatile solvents.

In order that a plasticiser may be effective it must be dissolved by or associate with the solid matter of which the film

is composed, since only under such conditions can a homogeneous film be obtained; a non-homogeneous film lacks mechanical strength. Considering the most usual pair of solid constituents of a cellulose lacquer, cellulose nitrate and ester gum, these have no solvent action on one another and in the absence of a common solvent a non-homogeneous film of inferior strength results; frequently sufficient medium or high-boiling solvent is retained to render the mixture homogeneous for a period, but if real permanence is to be obtained it is necessary to have present a plasticiser which is a solvent for both the cellulose ester and resin. It should also be realised that the vapour pressure of the plasticiser is reduced if it is actually dissolved by the cellulose ester or other solid ingredient, and it is therefore more definitely fixed than when not in solution; furthermore, within limits, the viscosity of a lacquer solution is generally reduced by the addition of a soluble plasticiser, but may be actually increased by a substance for which the cellulose ester is not a solvent.

If to a solid cellulose ester a solvent be added gradually, the solvent first associates with the solid causing it to gel; this phenomenon is best regarded as an absorption of the solvent by the cellulose ester, and the capacity of being thus absorbed or dissolved is an essential property in a plasticiser. If the addition of the solvent be continued, a region is reached in some cases in which two layers are formed, one layer consisting of solvent dissolved in the cellulose ester and the other of the cellulose ester in the solvent. The point at which this separation begins represents the limiting amount of plasticiser which can be used having regard merely to this consideration. If such a mixture having the two layers be heated, these layers will merge at a certain temperature, the "critical solution temperature," but on cooling the two layers will again form. With some mixtures the critical solution temperature is below that normally obtained in the atmosphere, in which case cooling is necessary if the phenomenon is to be observed (*cf.* p. 2). The phenomenon is dependent on the nature of both the solvent and the cellulose ester.

It follows, therefore, that whereas some plasticisers can be used in any proportion with a cellulose ester without showing any phenomena due to lack of homogeneity, others may give rise to cloudy or opaque films or to films which exude the plasticiser (synæresis). It is even possible to simulate

the effect of a solid white pigment by using a sufficient excess of a plasticiser, such as amyl benzoate, with celiulose acetate. The opinion is widely held that solid plasticisers, such as tri-phenyl phosphate, are unsuitable as plasticisers, since they tend to crystallise out of the film ; this is only true when the critical solution temperature is above the atmospheric temperature and the proportion of plasticiser is in excess of that which can be held in stable solution at atmospheric temperature. If this proportion be exceeded the system is unstable and the plasticiser, be it a solid or a liquid, may separate. Solids such as tri-phenyl phosphate under such conditions give cloudy films having a wax-like deposit on the surfaces, while liquids, such as amyl stearate and castor oil, give oily deposits. When such undesirable phenomena occur the remedy is to reduce the proportion of the particular plasticisers or to add another plasticiser, the critical solution temperature of which is well below the atmospheric.

The solvent power of plasticisers for cellulose esters or *vice versâ*, as some prefer to regard the phenomenon, varies considerably and is of considerable significance in certain directions : if dilution ratios be regarded as measures of the solvent powers certain conclusions may be drawn. Plasticisers possessing high dilution ratios permit the use of large propotions of non-solvent resins, such as ester gum, or similar non-compatible diluent than will those having low dilution ratios : they also are the more effective in preventing cotton blush. Plasticisers have a marked influence on the gloss of a film and on the flowing properties of a cellulose ester solution, particularly on the secondary flow ; this property is largely bound up with the viscosity of the solution in the later periods during drying and the viscosity in turn is largely a function of the solvent powers of the plasticiser. It follows that plasticisers having high dilution ratios are the better for imparting gloss, for the elimination of brush marks and for the ease with which a mass may be moulded under heat and pressure.

The following table gives the relative dilution ratios of the more commonly used plasticisers :—

Plasticiser.	Dilution Ratio to Toluene with ½ sec. Nitro Cotton. H.X. 45 I C.I.
Trituryl phosphate	24·0
Dibutyl tartrate	10·65
Diamyl tartrate	9·8

Plasticiser.	Dilution Ratio to Toluene with ½ sec. Nitro Cotton. H.X. 45 I.C.I.
Tributyl citrate	4·9
Triethyl citrate	3·9
Tricresyl phosphate	3·25
Diethyl phthalate	2·95
Butyl lævulinate	2·95
Dibutyl phthalate	2·8
Acetophenone	2·7
Dibutyl oxalate	2·6
Diamyl phthalate	2·3
Butylene glycol diacetate	2·3
Dimethyl phthalate	1·9
Benzyl lævulinate	1·6
Cyclohexyl lævulinate	1·4
Triacetin	0·9
Glyacol	0·9
Diacetin	0·35
Sipalin A.O.M. Sipalin M.O.M. Barkite Barkite B. Benzyl alcohol Benzyl benzoate Cyclohexanyl phthalate Butyl acetyl ricinoleate Butyl stearate Castor oil	Little or no solvent action under the conditions of the test.[1]

The proportion of plasticiser which should be used in a cellulose ester film varies not only with the plasticiser but also with the effects it is desired to procure. The chief effects which are governed by the proportion of plasticiser are :—

1. Plasticity.
2. Tensile strength.
3. Gloss.
4. Adhesion.
5. Elimination of volatile solvent.
6. Prevention of cotton, gum and water blushes.

No very definite quantitative information appears to exist on these aspects, and it is therefore only possible to make generalised approximate statements.

Small proportions of plasticisers initially increase the elasticity and tensile strength of cellulose ester films, which, in the case of plasticisers of the type of tricresyl phosphate and dibutyl phthalate, reach a maximum value with about 20 per cent. of plasticiser,[2] the plasticity and tensile strength thereafter diminishes with increasing proportion ; maximum gloss is also reached with similar proportions. A somewhat higher proportion is required to cause the ready elimination of residual volatile solvent, while still higher proportions favour adhesion, stability and the ease of application of the lacquer. The maximum proportions which can be used in the absence of resins are indicated in Appendix III.

Plasticised films subjected to tension exhibit elastic or reversible stretch until a certain tension is applied at which plastic or non-reversible stretch occurs. Highly plasticised films have, in general, a short region of elastic and a long region of plastic stretch before fracture occurs, whereas non- or insufficiently plasticised films exhibit a longer region of elastic stretch and little or no plastic stretch, but more force is required to produce a given amount of stretch in the non-plasticised film : colloquially it has less " give."

The fundamental function of a plasticiser is to increase extensibility, but while plasticisers effect this they also decrease elasticity and increase plasticity—that is, they decrease the reversible elongation or stretch and increase the non-reversible : the degree to which these two types of elongation are affected varies considerably with the plasticiser. Although no hard and fast demarcations can be made the plasticisers, in respect of this effect, may roughly be divided into three classes [2] :—

1. Those which permit, to a large extent, the retention of the original elasticity of the non-plasticised film while imparting considerable plasticity or extensibility—viz., camphor, tricresyl phosphate, diphenyl diethyl urea and p. toluene sulphanilide.

2. Those which make the film highly plastic and sacrifice elasticity—viz., triacetin, amyl oxalate and tributyl phosphate.

3. Those intermediate between these extremes—*e.g.*, the phthalates, sipalins, castor oil.

The tensile strength of cellulose nitrate is affected in varying degrees by plasticisers. Van Heuckeroth [3] quotes the following figures for cellulose nitrate films plasticised with

50 per cent. of various plasticisers under conditions of application similar to those obtained in factory practice. He remarks that " tensile strength should not be stressed too much, as different conditions and varying lengths of time of ageing of the films will influence the results greatly, and in some cases may invert the order thereof."

Plasticiser	Tensile Strength.
No plasticiser 1	581
No plasticiser 2	556
Diphenyl phthalate	470
Dimethyl phthalate	447
Tricresyl phosphate	382
Diphenyl diethyl urea	378
Triphenyl phosphate	363
Diethyl phthalate	348
Toluene ethyl sulphonamide	307
Castor oil	252
Diamyl phthalate	240
Dibutyl phthalate	229
Butyl acetyl ricinoleate	223
Tributyl phosphate	211
Butyl stearate	203
Ethyl acetyl ricinoleate	192

References

[1] DURRANS and DAVIDSON. *Chem. and Ind.*, 1936 ; 162T.
[2] JONES and MILLS. *Chem. and Ind.*, 1933 ; 251T.
[3] VAN HEUKEROTH. Nat. Paint Varnish Lacquer Ass. Circular 485 (1935).

CHAPTER IV

SOLVENT BALANCE

A CELLULOSE lacquer consists usually of :—

1. A cellulose ester,
2. A resin,
3. A solvent of high vapour pressure,
4. A solvent of medium vapour pressure,
5. A diluent,
6. A plasticiser, and
7. A pigment or dye ;

with the last item we are not here concerned.

We have to examine the general conditions which apply and the phenomena which may arise when a solution such as that indicated above, or variables of it, evaporates.

In order to prevent the occurrence of phenomena known technically as " chilling," " gum blushing," " cotton blushing," and the like, it is necessary to control the order and the degree in which the various liquid components of a lacquer evaporate. There is no great difficulty in effecting such control when the cellulose ester and the resin are both soluble in the solvents employed, such as is the case with solutions of cellulose nitrate and ester gum in ethyl, butyl or amyl acetates, or in certain " Two-type " solvents [1] such as diacetone alcohol, or ethyl lactate, which possess groups having specific solvent properties for cellulose nitrate and resins. The sole defect likely to arise in such instances is that of " chilling " or " water blush," which is due to the lowering of the temperature of the film and of the air in its immediate neighbourhood to below the dew point of the atmosphere, this being caused by the excessively high rate of evaporation of a too volatile solvent. Chilling is often characterised by the early appearance of cloudiness or opacity in the still liquid film, this opacity, if not excessive, generally disappearing on warming or long standing.

If to a solution of cellulose nitrate and resin in a single solvent there be added a diluent, it is necessary to use a diluent the rate of evaporation of which is greater than that of the solvent in order to ensure that at no instant shall the ratio

of diluent to solvent be in excess of that at which either the cellulose nitrate or the resin begins to be thrown out of solution, *i.e.*, the dilution ratio at any particular concentration shall not be exceeded. These limits can be experimentally investigated by determining the dilution ratios for a series of final concentrations (see p. 5), and it will be found that, in general, the greater the concentration of the solids the smaller the ratio of diluent to solvent permissible. If, therefore, it is desired to use the maximum proportion of diluent it is advisable to employ a mixture of solvents whose boiling-points increase progressively, *e.g.*, ethyl, butyl and amyl acetate, but it should be borne in mind that increase in boiling-point is generally accompanied by decrease in solvent power (*cf.* Table of Dilution Ratios, p. 6). For the same reason it is undesirable to use mixed diluents, a single diluent of suitable vapour pressure being the best, the vapour pressure of this diluent being greater than that of any of the solvents, but sufficiently low to avoid chilling.

If a volatile diluent be mixed with a volatile solvent, the boiling-point of the mixture may be lower than that of either (see Chapter VI), and the ratio of diluent to solvent which evaporates may in consequence be affected. Such azeotropic mixtures, as they are termed, are of quite common occurrence, many instances being given in Part II. Azeotropic mixtures tend to cause chilling and necessitate the incorporation of a larger proportion of the solvent of higher boiling-point; further, the ratio of solvent to diluent which evaporates may be such that the solvent is removed in greater quantity than is the diluent, and precipitation may in consequence occur. The use of a diluent of considerably lower boiling-point than that of the lowest-boiling solvent will avoid or mitigate this effect. Azeotropic mixtures appear occasionally to have solvent powers different from what would be normally expected, but the phenomenon is as yet not clearly demonstrated. It would seem advisable to avoid the simultaneous use of diluents and low-boiling solvents, which give rise to azeotropic mixtures.

Solvents vary in solvent power, diluents vary in precipitating power; indeed, the demarcation between solvents and non-solvents is not clearly defined. Petroleum hydrocarbons generally precipitate cellulose nitrate from its solutions more readily than do benzenoid hydrocarbons, and these more

readily than the aliphatic alcohols; the members of each class differ, more or less progressively, from one another, but the difference is not so marked. The nature of the cellulose nitrate or acetate or the resin has a profound effect; some cellulose nitrates, for instance, being soluble in ethyl alcohol while others are completely insoluble.

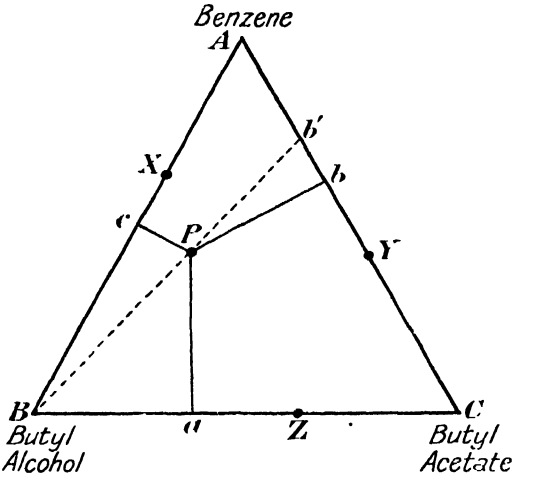
If it is desired to produce a solution of cellulose ester and resin and to use two different solvents, each of which is a solvent, for only one of the solids respectively and not for the other, it becomes a matter of considerable difficulty to adjust the solvent mixture satisfactorily. This is particularly the case with cellulose acetate-resin solutions. On mixing a solution of a cellulose ester with a solution of a resin, precipitation of one or both of the solids may partially occur depending on the tolerance (see Dilution Ratios) of one solvent for the other with respect to the dissolved solids. If, however, precipitation does not occur on mixing, it may do so during the subsequent evaporation owing to the limits of toleration being exceeded, especially if the rates of evaporation of the two solvents be widely different. The effects produced by this cause are known respectively as "cotton blush" and "gum blush," and are characterised by the appearance of cloudiness or opacity shortly before the film sets, the opacity persisting permanently.

When it is not feasible to adjust the evaporation rates of the two solvents satisfactorily, these types of blush can be avoided by using a small proportion of a high-boiling solvent, which is a solvent for both the cellulose ester and the resins; the plasticiser can often fulfil this function.

Another phenomenon, the reason for which is not clearly understood, is the appearance of a haze when separate solutions of cellulose ester and resin in the same solvent are mixed. Instances of this are found with solutions of cellulose nitrate and ester gum in diacetone alcohol and of cellulose nitrate and kauri in ethyl lactate. In the former case the haze can generally be removed by adding a small quantity of benzyl alcohol or cyclohexanol, and in the latter case of butyl alcohol or acetate or of ethylene glycol monoethyl ether.

Solvents which are readily miscible with water present a specific aspect. Water may be regarded merely as a non-solvent diluent such as are the hydrocarbons and the alcohols; there is no essential difference. Water has been used to

replace the more expensive organic diluents in conjunction with water-miscible solvents, such as the ethylene glycol mono-alkyl ethers, diacetone alcohol and ethyl lactate, but the device has no technical value on account of the powerful tendency of water to precipitate resins and cellulose esters and to produce the so-called " orange-peel " effect ; this effect, which has been likened to the pimply surface of an orange, can be caused by an excessive rate of evaporation of the solvent relatively to that of the diluent. It is frequently noticed on sprayed films when the solvent has evaporated too freely during transit from the spray gun nozzle to the coated surface causing a too rapid increase in viscosity. If to a lacquer in which the amount



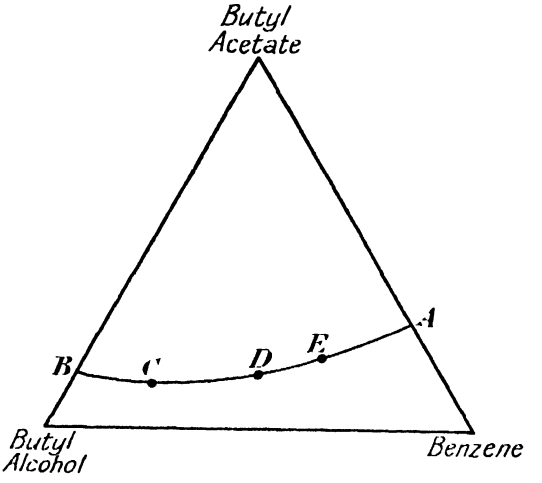
CURVE 1.

of diluent is on the border line of the maximum permissible, more diluent be added, be it hydrocarbon, alcohol or water, precipitation will occur. This is precisely what occurs when chilling takes place, the non-solvents are in excess locally, generally on the surface of the film. If the lacquer contain a sufficient excess of solvent, chilling will not occur. Where the limiting proportion of diluent is present the introduction of more diluent, in the form of water, by deposition from the atmosphere, will cause precipitation of chilling. Under such circumstances it is desirable to have a solvent which is not capable of dissolving water, as any precipitation is then limited to the surface and is transient.

Proportions of water up to about 1% increase the solvent powers of many solvents and diminish the viscosities of their

solutions, hence the demand for completely anhydrous solvents is probably unsound.

In order to visualise the limiting proportions of a system of three solvent-diluent components use may be made of triangular co-ordinate graphs.[2] The triangular co-ordinate graph system is represented by an equilateral triangle, each side of which is divided into an equal number of equal divisions, usually one hundred, so as to represent percentages. In the example shown here (curve 1) the apexes A, B, and C represent respectively 100% of three pure components such as (A) Benzene ; (B) Butyl alcohol ; (C) Butyl acetate. A point X along AB represents a mixture of BX% of benzene and



CURVE 2.

AX% of butyl alcohol, a point Y along AC one of CY% of benzene and AY% of butyl acetate, while Z along BC represents CZ% of butyl alcohol, and BZ% of butyl acetate. A point P within the triangle represents the composition of a mixture of all three, the percentage of each being given respectively by the lengths of the perpendiculars from P to the sides of the triangle opposite to the apex representing 100% of the particular component, thus P*a* represents the percentage of benzene, P*b* that of butyl alcohol, and P*c* that of butyl acetate, the sum of P*a*, P*b* and P*c* being one hundred. The ratio of benzene to butyl acetate is found by joining B and P and extending the line to cut the line AC at *b'*. In a similar manner the ratio of benzene to butyl alcohol and of butyl alcohol to butyl acetate can be found.

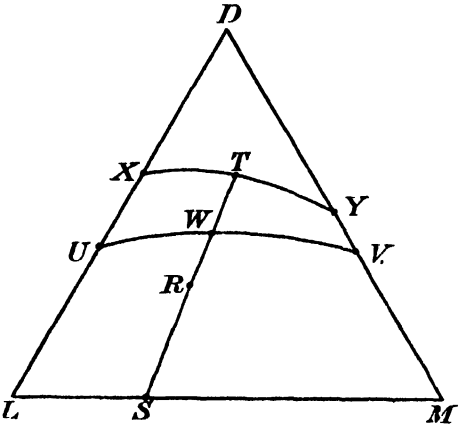
A practical application of the method may here be given. Suppose it is desired to determine the solubility limits of a given percentage of cellulose nitrate in mixtures of butyl acetate, butyl alcohol and benzene. A series of determinations is made of the ratio of butyl acetate to diluent (butyl alcohol, benzene and mixtures of these). Thus the point A (curve 2) represents the composition of a mixture of butyl acetate and benzene that will just dissolve the given percentage of cellulose nitrate ; the point B the equivalent mixture of butyl acetate and butyl alcohol, while C, D, and E represent the composition of mixtures of all three. Any mixture the composition of which is represented by a point below the line AEDCB will not dissolve the given percentage of cellulose nitrate, whilst any mixture whose composition falls into the area above the line will give complete solution. The knowledge thus obtained allows other factors to be correlated, for instance, that of cost or rate of evaporation. Thus, although benzene is cheaper than butyl alcohol it has greater precipitating power, and a larger proportion of butyl acetate is therefore required than if some of the benzene had been replaced by the more costly diluent butyl alcohol ; the cheapest mixture may, for instance, be represented by the point E.

Triangular co-ordinates can similarly be used to visualise the change in composition of a three-component solvent mixture on evaporation, and to determine if at any time during the evaporation the composition could be such that precipitation of the cellulose nitrate could occur. Other uses to which the system may be put are the determination of solvent compositions for mixtures of a cellulose ester and a resin, for the variation of viscosity [3] and of cost.

As a further illustration of the practical application of triangular co-ordinates, let it be supposed that it is desired to produce the cheapest possible lacquer having 10% of a certain quality of cellulose nitrate dissolved in a mixture of " low boiler," " medium boiler " and diluent ; the lacquer to have a definite viscosity and blush resistance. Let the apex D represent 100% of diluent, L represent 100% of " low boiler " and M 100% of " medium boiler." Determine the dilution ratio of the " low boiler " and diluent for a mixture that will just dissolve the 10% of cellulose nitrate, let X be the point on the line DL which represents this mixture, similarly determine the point Y for the " medium boiler " and diluent.

Within certain limits of accuracy a straight line XY represents all mixtures of the solvents and diluent which will just dissolve 10% of the cellulose nitrate. In general, XY will not be a straight line, but will be curved towards D. If greater accuracy is required the curve of the line may be found by determining the dilution ratios for known mixtures of the two solvents with the diluent. The area DXY now represents mixtures which will not dissolve the requisite proportion of cellulose nitrate and such mixtures must therefore be left out of further consideration.

Next consider one of the other properties which it is wished to establish in the lacquer, the resistance to chilling



CURVE 3

for instance. Having decided what are the limiting conditions of humidity, temperature and rate of drying that the lacquer must withstand without chilling, determine by systematic trial and error tests what ratio of " low boiler " and " medium boiler " just gives signs of chilling under the prescribed conditions and obtain the point S on the line LM which represents this ratio ; repeat the tests with mixtures of all three liquids, the compositions of which lie on the line XY, and obtain the point T. Join S and T. Here again, ST is not necessarily a straight line, depending largely on the possible formation of low-boiling azeotrophic mixtures ; the determination of points such as R may be advisable. The region XLST represents solutions which will chill under the given conditions, and can therefore be eliminated from further consideration. Consider now a third property,

viscosity for example. Determine by any of the well-known methods the composition of the mixture of " low boiler " and diluent which gives the desired viscosity with 10% of the cellulose nitrate and obtain the point U on the line I.D ; similarly determine the point V, using the " medium boiler " and diluent. Joint U and V. The curvature of the line UV may be determined by actual test with mixtures, the composition of which are represented by points on the line ST, for instance W. Should either U or V fall above X or Y respectively it may still be possible to produce a lacquer having the desired properties, since the lines UV and XY may cross. It may quite well happen that the desired viscosity cannot be obtained with mixtures of the " low boiler " and diluent without precipitation occurring. Should this be so it will be necessary to make viscosity determinations with mixtures lying close to the line XY, but considerable inaccuracy may arise, as there may be somewhat abrupt changes of viscosity as the insoluble region is approached. Having determined the viscosity line UWV, any third property, such as cost or " flow," can be determined along the line VW. It is easy, for instance, to calculate the cost of lacquers represented by points along the line WV, the point W generally representing the cheapest mixture of solvents. Flow may be measured as the viscosity after a certain proportion of the solvent has evaporated, and similarly determined along VW.

The subsequent incorporation of resin and plasticiser into the lacquer will have some effect and may necessitate a slight adjustment.

Certain short cuts may be made ; thus the determination of the line XY is not absolutely necessary, and the point W may be found without determining S and T, but the limitations of the lacquer cannot then be visualised so well.

References

[1] KEYS. *Ind. Eng. Chem.*, 1925, p. 1120.
[2] HOFFMAN, REID and STOPPEL. *Ind. Eng. Chem.*, 1928, p. 431.
[3] COCHRANE and LEEPER. *Chem. and Ind.*, 1927, p. 118T.

CHAPTER V

VISCOSITY

VISCOSITY may be broadly defined as " resistance to flow," and is of considerable technical importance in connection with lacquers.

For many years it was not possible to make satisfactory lacquers with the cellulose nitrates then available, since those nitrates gave solutions of excessively high viscosity when prepared in a state sufficiently concentrated to ensure films of the desired thickness and strength. Many, more or less successful, attempts were made to reduce this viscosity by employing various solvents, but this generally resulted in introducing other undesirable characteristics. It was not until the introduction of the low viscosity cellulose nitrates, such as the well-known " half-second cotton," took place, that the widespread use of such lacquers became possible ; even now it is common practice to " load " the lacquer with resins for the purpose, among others, of giving " body " to a film without of necessity producing unduly viscous solutions.

The viscosity of a lacquer may be adjusted in several ways ; thus different grades of cellulose nitrates may be employed, these being available in various viscosities, or the viscosity may be varied by suitable choice of solvent or solvent mixture. Viscosity and vapour pressure are apparently to a considerable extent concomitant properties, the greater the vapour pressure of a solvent the lower the viscosity of its solutions.

The following table [1] shows the percentage of dry $\frac{1}{2}$-sec. cellulose nitrate which can be dissolved in various solvents to give solutions having a viscosity of 10 secs. (Cochius) :

Acetone	15%
Ethyl acetate	12%
Amyl acetate	9%
Butyl propionate	8%
Propyl butyrate	7·5%
Diacetone alcohol	4%
Cyclohexyl acetate	4%

The viscosity of a solution may in general and within limits be increased by the substitution of part of the solvent by a non-solvent, but inasmuch as the admixture of a non-solvent with a solvent sometimes gives a mixture having increased solvent powers, no hard and fast rule can be formulated ; for this reason the partial substitution of a non-solvent for a solvent sometimes initially results in a decrease of viscosity, whilst the continued replacement of the solvent beyond a certain proportion causes an increase, and finally gelation or precipitation of the cellulose nitrate.

With a given cellulose nitrate the viscosity of its solution in ether alcohol mixture is dependent on the ratio of ether to alcohol,[2] and reaches a minimum at a definite ratio. Indeed, the viscosity of a solution of cellulose nitrate is fundamentally bound up with the nature of the solvent, but in general it may be said that the greater the solvent power of a liquid the lower the viscosity of its solutions.[3] The same may be said of solutions of cellulose acetate. Thus with mixtures of acetone and alcohol the minimum viscosity is obtained when the ratio of alcohol to acetone is about one to six [4], with benzene and acetone, when the ratio is one to five ; whilst a mixture containing one of alcohol, three of benzene, and six of acetone gives solutions of the lowest viscosity.

Viscosity determinations are of considerable value for the purpose of selecting and standardising the cellulose ester or ether which is to be used to prepare a lacquer and also for standardising the resultant lacquer. A lacquer destined for use in a spray gun should initially be less viscous than a brushing lacquer, and in both cases it is of importance to have a knowledge of the progressive variation in viscosity consequent upon the partial evaporation of the solvents.

The viscosity of a cellulose-ester solution does not increase proportionately with the concentration of the solution except at extreme dilutions ; with concentrated solutions a small increase in the content of cellulose ester greatly increases the viscosity [6] ; between concentrations of 10% and 20% the viscosity increases geometrically.[5] It follows therefore that in order to adjust the viscosity of all but very thin solutions, it is better to vary the proportion of cellulose ester than to alter the composition of the solvent, since the latter practice may cause some undesirable effect, such as " blushing," or bad " flow."

When it is desired to reduce the viscosity of a solution by means of " thinners," these should have the same composition as that of the liquids in the original mixture : if, however, a lacquer has become viscous by reason of the evaporation of part of the solvent, it is then necessary to use thinners having a larger proportion of the low-boiling constituents, and in order to use the correct amount of these it is best to analyse the lacquer first and then to make the necessary additions.

The viscosity of cellulose-ester solutions, the solvents of which have not been allowed to evaporate, becomes less with age, but subsequent agitation of the solution causes the viscosity to return ultimately to its original value.[7] The presence of basic substances accelerates the reduction of viscosity with age ; sunlight and heat have the same effect, but water and urea appear to have a stabilising effect.

It is possible to obtain considerable control over the viscosity or flow of a lacquer during all stages of its drying. In general, it may be postulated that solvents of low boiling-point yield solutions of low viscosity, and that increasing boiling-point is accompanied by increasing viscosity. This is particularly noticeable in a homologous series such as methyl, ethyl, butyl and amyl acetates. The phenomenon may be ascribed to the change in molar concentration which must accompany the change in the size of the molecule ; thus there is a larger number of molecules of ethyl acetate in a given weight than in the same weight of amyl acetate. The molecular proportion of ethyl acetate is therefore the larger in a solution containing a given percentage of cellulose nitrate.

As has been pointed out above, a small increase in the cellulose-ester content of a lacquer greatly increases the viscosity. It follows from this that when a solvent evaporates from a solution of cellulose ester dissolved in a single solvent the increase of viscosity is relatively slow at first, but continues to increase at an ever-increasing rate up to a point determined by the concomitant slowing up of the rate of evaporation of the solvent ; thus the rate at which the viscosity increases is at first comparatively slow, becoming more rapid, and then slower and slower. By employing a mixture of low and medium boilers, the rate of evaporation during the period in which the increase of viscosity is rapid may be slowed and the rapid increase of viscosity slowed in consequence. This is a desirable effect to obtain, since lacquers which increase in

viscosity too rapidly flow badly, and are difficult to manipulate. It is necessary, however, to employ some quantity of low-boiling solvent since " medium boilers " and " high boilers " do not lead to a sufficiently rapid increase of viscosity after application ; the flow is in consequence too protracted and the film develops waves or otherwise varies in thickness.

The diluent may affect the changes in viscosity considerably. The viscosity of a solution may, in general, and within limits, be increased by substituting diluent for solvent ; but since the addition of a diluent may occasionally increase the solvent power of a solvent, the viscosity sometimes initially decreases on adding a diluent, while a further quantity of diluent results in increased viscosity, and finally in precipitation of the cellulose ester. The converse effects may be produced when a low-boiling diluent evaporates from a lacquer, the solvents of which are medium or high-" boilers," namely, an initial increase of viscosity followed by a diminution. In general, if the " low boiler " and diluent evaporate at the same rate the viscosity of the remainder will increase, but it is possible to maintain a more or less constant viscosity over a short period of evaporation by using a diluent which evaporates more rapidly than the " low boiler."

The change of viscosity in the later period of the drying of a film may be slowed by employing high-boiling solvents, this is commonly done with brushing lacquers designed for amateur use, the prolongation of the " semi-fluid " state allowing ample time for manipulation. Such lacquers tend, however, to develop waves or other unsightly defects besides yielding films which lack permanency. It is better to rely on " medium boilers " and plasticisers to obtain delayed drying.

The viscosity during the final stages of drying depends largely on the proportion of plasticiser and its plasticising power as contrasted with its power of imparting elasticity. High gloss, which is to a large extent the result of prolonged " secondary flow " (see p. 9) can be obtained by plasticisers having high plasticising power.

The functions of the various classes of solvents may be summarised as follows :—

(1) " Low boilers " of high solvent power to enable concentrated solutions of low viscosity to be prepared and to obtain quick initial drying and increase of viscosity.

(2) " Medium boilers " to check the rate of evaporation

and thus to reduce defects caused by excessive rates and also to impart good flowing properties.

(3) " High boilers " to protract the period of drying for long periods when necessary, and to impart good brushing properties and high gloss.

(4) " Plasticisers " to knit all the solid constituents into a homogeneous whole, to impart flexibility, gloss and permanence, and to reduce brittleness.

(5) " Diluents " to reduce cost, to control viscosity, and, occasionally, to dissolve resins.

The viscosity of solutions of resins follows on quite different lines to those of the cellulose esters. The viscosity of solutions of the former is practically constant with solvents of a homologous series, such as benzene, toluene and xylene, or di-, tri-, and perchloroethylene.[8] The viscosity depends markedly on the constitution of the solvents, being much greater with saturated than with unsaturated substances. The presence of a hydroxyl group in the solvent appears to increase the viscosity. Drummond [9] divides synthetic resins into two classes—those soluble in " polar " solvents, such as alcohols or ketones, which contain hydroxyl or carbonyl groups ; and those soluble in " non-polar " solvents, such as hydrocarbons. The former class includes phenolic resins, acrolein resins and glyceryl-phthalate resins, whilst in the latter class are cumarone, albertol, oil-soluble phenolic resins, and naphthalene-formaldehyde resins.

The measurement of the viscosity of lacquers is obviously of considerable technical importance, and much attention has been given to the methods and instruments which may be employed. The instrument of greatest utility for lacquers is known as the " falling sphere viscometer." [10] The method of its operation has been exactly standardised by the British Standards Association,[11] and consists, briefly, in measuring the time of fall of a clean steel ball between two points in a vertical glass tube filled with the solution, the temperature of which has been carefully adjusted. For details of the test the reader is referred to British Standard Specification No. 188, 1937.

Other methods which should be mentioned are those of Engler [12], Ostwald [13], Cobenzl [14], Stern [15], Ford [16], Holde-Ubbelohde [17], Kampf [18], Vogel-Ossag [19] and Cochius [20].

The following figures have been quoted [21] for the com-

parative viscosities of 15% solutions of 4 sec. N.C. in various solvents :

Acetone	20 secs.
Methyl acetate	42 ,,
Ethyl acetate	92 ,,
Amyl acetate	127 ,,
iso-Butyl acetate	131 ,,
Butyl glycol	200 ,,
Methyl glycol	225 ,,
Cyclohexanone	299 ,,
Methyl cyclohexanone	304 ,,
Ethyl lactate	397 ,,
Butoxyl	426 ,,
Diacetone alcohol	610 ,,
Butyl glycollate	625 ,,

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CHAPTER VI

VAPOUR PRESSURE AND EVAPORATION RATES

IT is not an exaggeration to say that all substances give off a vapour and therefore exert a vapour pressure. The vapour pressures of substances vary to a wide extent, and that of most solids is quite inappreciable at ordinary temperatures to all but the most delicate instruments. The vapour pressure of most liquids at ordinary temperatures is confined to quite a limited range, viz., pressures up to one atmosphere, but the variation within this range of the vapour pressure of solvents is of paramount importance, since it is one of the prime factors governing the rate at which evaporation takes place.

It is necessary to be able to control, in some degree, the rate at which the liquid medium of a lacquer evaporates in order :

1. To prevent the deposition of water from the atmosphere.
2. To control the " flow " of the lacquer.
3. To prevent the premature precipitation of any ingredient which might cause the film to be non-homogeneous.
4. To prevent undue contraction of the film.

For any given single solvent the rate of evaporation is governed by several factors :

1. The vapour pressure of the liquid at the temperature under consideration.
2. The rate at which heat is supplied.
3. The conductivity for heat of the liquid.
4. The specific heat of the liquid.
5. The latent heat of evaporation of the liquid.
6. The degree of association of the molecules.
7. The surface tension of the liquid.
8. The molecular weight of the liquid.
9. The humidity of the atmosphere.
10. The rate at which the vapour adjacent to the liquid is removed.
11. The vapour density of the solvent.
12. The solvent power of the solvent.

With mixtures the rate of evaporation is further governed by :

1. The molecular attraction of one component by another.
2. The depression of the vapour pressure of one component by another.
3. The viscosity, if the solute be a colloid.

The problem is obviously one of considerable complexity. It may be possible at some future date accurately to evaluate the influence of all these factors and thus to control the manner in which a lacquer shall dry, but at present it is only possible to form a rough judgment, and it is necessary to allow a large margin of safety in order to accommodate conditions over which it may not be possible to have control.

Many essential data regarding the various factors enumerated above are missing, and it is as yet very difficult to apply technically such information as is available.

The first attempt in this direction was to classify solvents as low, medium and high " boilers," according to their boiling-points, and although the classification was admittedly unsatisfactory it permitted some degree of control to be obtained. It was customary to consider as " low boilers " those solvents with boiling-point below 100° C., as " medium boilers " those boiling from 100° up to an indefinite temperature above the boiling-point of amyl acetate, *e.g.*, about 150°, whilst those of still higher boiling-points were termed " high boilers," these last merging into the " plasticiser " class, which included substances like benzyl alcohol.

It was soon realised that boiling-points represent the temperatures at which the vapour pressures of liquids are the same as the atmospheric pressure and do not accurately correspond to their vapour pressures at the temperatures at which lacquers are ordinarily used, namely, atmospheric or slightly higher. Thus the examination of vapour pressure-temperature curves shows that in some instances the curves relating to two substances actually cross and that the relative vapour pressures vary with the temperature irrespectively of the boiling-point. This phenomenon is generally occasioned by the molecules of one of the liquids being " associated " at normal temperatures, *i.e.*, two or more molecules are loosely combined ; this association causes a diminution in the vapour pressure of the substance, but it breaks down progressively as the temperature rises. The phenomenon is observed particu-

larly among those substances having hydroxyl groups, as in the case of alcohols and acids. It is for this reason that alcohols of quite low boiling-point, such as propyl alcohol, evaporate more slowly than some of their esters of higher boiling-point, such as propyl acetate. Another instructive example is that of the closely similar substances cyclohexanone and cyclohexanol, these boil at nearly the same temperature (150°–160°), but cyclohexanone evaporates ten times as rapidly as cyclohexanol.

Not only may a single liquid form associated molecules, but liquids on mixing sometimes associate one with another. In the latter case the simplest relations have been found to hold.

The vapour pressure of two liquids, A and B, which are miscible in all proportions and do not react chemically with one another or associate, is given by the expression :—

$$100\,P_{a+b} = M_a P_a + (100 - M_a)\,P_b$$

where M_a is the molecular percentage of liquid A,

P_a and P_b the respective vapour pressures of A and B at the given temperature, and

P_{a+b} the vapour pressure of the mixture at the same temperature.

If inter-molecular attraction between the two liquids exists. the mixtures have abnormal vapour pressures, either higher or lower than the values given by the above equation. Thus in the case of acetone and chloroform the gradual addition of one of them to the other causes a diminution of the vapour pressure until a minimum is reached, and then an increase until the vapour pressure of the one in excess is reached. The same phenomenon occurs with methyl acetate and chloroform, but it is not common with organic solvents. It is more usually found that the gradual addition of one solvent to another causes the vapour pressure progressively to increase until the maximum is reached, and thereafter to diminish. The mixture having the maximum vapour pressure (minimum boiling-point) is termed an azeotropic mixture of minimum boiling-point, and has, of course, a lower boiling-point than either of its two components. This mixture of minimum boiling-point is not necessarily of the same percentage composition as that having the maximum vapour pressure at ordinary temperature [1] ; thus the composition of

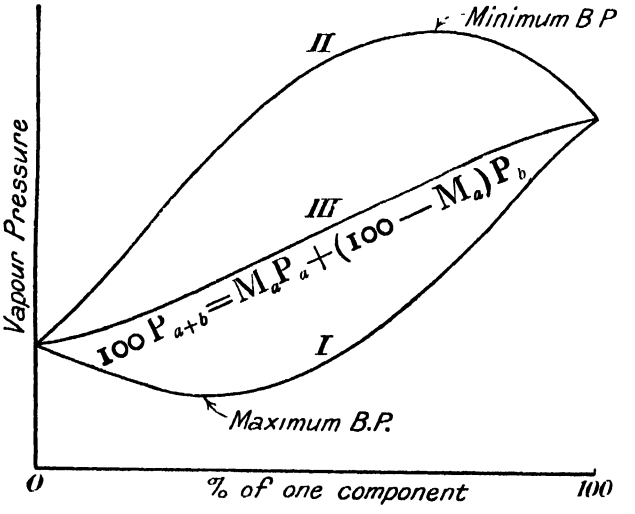
mixtures of minimum boiling-point of benzene and alcohol varies with the pressure, as shown in the following table [2] :—

Pressure.	B.P. of Azeotropic Mixture.	Percentage Alcohol.
mm.	°C	
760	68·25	32·4
570	60·0	28
380	49·9	26
241	35·0	23·3
200	34·8	22

If these figures are extrapolated to normal temperature the proportion of alcohol is found to be about 20%.

It should be noted that the boiling-point of the azeotropic mixture is lower than that of either component at the same pressure.

If the vapour pressure of mixtures of the two liquids A and B be plotted against the composition of the mixture, it is found that the curve takes one of three forms, as shown in the diagram below. Form III is that normally shown by non-



associated liquids such as mixtures of ethyl acetate with propyl alcohol ; it is practically never a straight line. Mixtures of maximum boiling-point, such as acetone with chloroform, give a curve of Form I, whilst mixtures of minimum boiling-point, commonly found, such as ethyl acetate with

ethyl alcohol, give Form II. Other types of curve are theoretically possible, but only one minimum or maximum can occur with substances that are miscible in all proportions.[3]

A number of instances are known in which three liquids form a mixture having a lower boiling-point than any of its components, *e.g.*, ethyl alcohol, chloroform, hexane, isopropyl alcohol, ethyl acetate, and cyclohexane. In all probability the number of components may be still greater but no actual observations appear to have been recorded.

The reason for the scarcity of azeotropic mixtures having more than two components seems to lie in the probability that for a system of three or more components each component must be capable of forming a binary azeotrope with each of the others separately, so that with an increase of but one in the number of components the chance of the formation of an azeotropic mixture comprising all the components is greatly lessened.

It has been shown [12] that the composition of the vapour arising from a mixture of liquids evaporating in free air may be profoundly influenced by minor modifications in the conditions and that the composition of the vapour under certain conditions may be different to that of the azeotrope at the same temperature.

In actual practice azeotropic mixtures have effect in several ways. The increase of vapour pressure which accompanies the formation of an azeotrope has a distinct influence on the flash-point of a mixture. The increased vapour pressure causes a greater quantity of solvent to be evaporated into the air space of a container at any given temperature than if no azeotrope were formed, and since the flash-point is largely governed by the proportion of inflammable vapour, the necessary proportion is reached at a lower temperature. Similarly the proportion for maximum explosivity (*cf.* p. 48) is reached at a lower temperature. The increase in vapour pressure will also cause the rate of evaporation to be greater and may result in " chilling " or other defects due to an excessive rate of evaporation ; furthermore, the deposition of water during " chilling " may give rise to ternary azeotropes which have generally still higher rates of evaporation. It is also possible that the formation of an azeotrope may affect the solvent power of a mixture.

The formation of an azeotrope affects the relative rates at

which the constituents of a mixture evaporate, since the azeotrope tends to evaporate as though it were a single substance. It is advisable, therefore, when using a non-solvent diluent to choose the solvent so that either no azeotrope is formed or if it be formed that it shall be one having a higher proportion of non-solvent than solvent, in order that the non-solvent may be removed more rapidly than the solvent; otherwise " cotton blush " or " gum blush " may occur if the concentration of these solids be too near to the saturation point of the mixture.

If no azeotrope is formed by two miscible liquids, the vapour pressure of the mixture is directly proportional to the relative amounts of the two liquids and their respective vapour pressures at the temperature under consideration, namely the normal atmospheric temperature. By adding a medium or high " boiler " to a low " boiler " we slow up its rate of evaporation more or less proportionally to the amount added. Theoretically a medium " boiler " will reduce the vapour pressure and consequently slow up the rate of evaporation of a low " boiler " more than will a similar weight of a high " boiler." A substance of low molecular weight is more effective than a similar mass of one of high molecular weight, since it is the number of molecules that matters, and mass for mass the substance of low molecular weight has the larger number of molecules.

If a layer of lacquer be allowed to evaporate, the rate at which the solvent leaves the solution slows progressively, the lacquer becomes more and more viscous, and the molecules of solvents diffuse more and more slowly to the surface from which evaporation takes place. At this stage the size of the solvent molecule is probably the prime factor governing the rate of evaporation, but vapour pressure still has some effect. Generally, large molecules and low vapour pressure are concomitant phenomena; substances the molecules of which are large evaporate more slowly than those having small molecules.

When a liquid evaporates it gives up energy and its temperature drops. In order that it may continue to evaporate, it is necessary to supply heat from an external source, otherwise the temperature would drop until evaporation ceased. The drop in temperature is governed by three factors, the specific heat and the latent heat of evaporation of the liquid,

and its conductivity for heat; of these factors the latent heat is the most important.

The latent heat of evaporation of a liquid can be found approximately by Trouton's formula.

Trouton found, in 1884,[4] that the amounts of heat required to evaporate quantities of different liquids taken in the ratio of their molecular weights are approximately proportional to their absolute boiling-points; in other words, the product of the molecular weight and the latent heat of evaporation is proportional to the absolute boiling-point, or expressed symbolically:

$$M \cdot H = C\,T,$$

where C is a constant (the value of which for normal liquids is 20 to 21, such liquids being hydrocarbons, esters, ethers and ketones, whilst for associated liquids such as alcohols and water the value is higher, being about 26), M is the molecular weight of the liquid, T the absolute temperature (°C. + 273), and H the latent heat of evaporation.

Methods have been devised for obtaining a measure of the "blush resistance" of solvents. One method is somewhat similar to that for measuring the solvent powers of solvents by determining their "dilution ratios," and consists in diluting the solvent with blush-inducing materials until a faint blush can be obtained under standardised conditions.[7]

The blush numbers found for certain solvents are as follows:—

Ethyl acetate, 85%	0
Ethylene glycol ethyl ether	0
Butyl acetate	1·05
Pent-acetate	1·75
Butyl propionate	1·75
Pentexel	2·00
Ethylene glycol butyl ether	3·90
Ethylene glycol ethyl ether acetate	4·00
Ethyl lactate	4·00

Another method [11] consists in estimating the degree of blushing of 10% solutions of cellulose nitrate under varying degrees of humidity.

Empirical evaluations of the lowering of the temperature of solvents on evaporation have been made by Gardner and

Parks [5] under more or less standardised but arbitrary conditions ; the results, however, seem to be of somewhat doubtful validity.

The lowering of temperature of a solvent evaporating in free air causes the air in its immediate neighbourhood to fall in temperature, and if the humidity of this air be sufficiently great a temperature below that of the dew-point may be reached and water will be deposited. If the solvent contain a substance insoluble in water, for instance, cellulose nitrate or resin, this deposition of water may cause their precipitation with the consequent formation of a white opaque film on the surface of the solution ; this effect is known as " chilling," or " blushing." If the solvent is one able to dissolve water to a considerable extent, such as ethyl lactate, diacetone alcohol, or ethyl alcohol, this chilling effect may be delayed, since the water may be dispersed throughout a greater depth of the solution. If, on the other hand, water is completely insoluble in the solvent no chilling can occur, since the water will merely deposit on the surface and not penetrate at all. It follows that a hygroscopic solvent is more likely to give rise to " chilling " than is a non-hygroscopic one (*cf.* p. 17).

It is frequently found that a lacquer, normally satisfactory, will " chill " in abnormally damp weather ; by determining the " dew-point " or humidity of the atmosphere it is possible to select a solvent composition suitable for the occasion ; the greater the humidity the greater the proportion of " high or medium boiler." The determination of the dew-point should be a regular factory practice.

Chilling is not unfrequently prevented by raising the temperature either of the lacquer or the air to a degree sufficiently high to prevent the dew-point being reached on subsequent evaporation ; another method is to " dry " the air either by chemical means, by compression, or by condensing out the water by cooling and reheating the " dry " air again before use. The compression method is the most convenient when the lacquer is to be applied by a spray-gun. Chilling can also be eliminated by diminishing the rate of evaporation, this being effected by enclosing the lacquered article in a more or less stagnant atmosphere partially charged with the vapours of the solvent.

Chilling which has taken place may disappear at a later period during the drying of a lacquer owing to the evaporation

of the water and the re-solution of the precipitated solid in the high-boiling solvent remaining. The addition of a solvent of high molecular weight, and hence of high boiling-point, is usually an effective method of eliminating a tendency to chilling in a lacquer, since the " high boiler " not only redissolves precipitated solids but also, as already shown, slows down the rate of evaporation of the low-boiling solvent to which the chilling is initially due.

A defect which sometimes accompanies the use of a spray-gun is that of a rough surface known as " sand-papering " or " pimpling " ; this is caused by the passage of too large a volume of air, caused commonly by the use of excessive pressures. The large quantity of air promotes such rapid evaporation of the low-boiling solvents that the lacquer reaches the " work " in a semi-solid or plastic state and is unable to flow sufficiently ; the remedy is to use either a lower air pressure or partly to replace the more volatile constituents with less volatile.

Cellulose lacquers usually contain both a cellulose ester and a resin, the latter being added for the purpose of imparting " body," gloss, hardness or adhesiveness to the resultant film. It is thus necessary that the solution should at all periods during its evaporation contain a sufficiency of solvent or solvents to keep in solution both the cellulose ester and the resin. Should the resin solvent by reason of its higher rate of evaporation fall below a certain proportion, the resin will begin to precipitate, the film will become cloudy and the defect known as " gum-blush " will arise. In a similar manner the cellulose ester may be precipitated and give rise to " cotton-blush."

It is thus desirable that the solvent of lowest vapour pressure should be a solvent for both the cellulose ester and the resin ; frequently the plasticiser will perform this function effectively ; indeed, it is a desirable property in a plasticiser that it should be a solvent for all the solid constituents.

The diluent used in any lacquer, being usually a non-solvent for either the cellulose ester or the resin or for both, should obviously evaporate at an early stage in the process, and therefore it should preferably be of the low-boiling type.

The rates of evaporation given on page 40 were determined by placing ½ c.c. of solvent on to filter paper and determining

	Evaporation Period.	Boiling Range.
Ethyl ether	1	34–35° C.
Methylene chloride	1·8	40–42° C.
Acetone	2·1	55–56° C.
Methyl acetate	2·2	56–62° C.
Ethyl acetate, 98/100%	2·9	74–77° C.
Benzol	3	80–81° C.
Benzine	3·5	67–100° C.
Ethylene chloride	4·1	81–87° C.
Isopropyl acetate	4·2	84–93° C.
Toluol	6·1	109·5–110·5° C.
Normal propyl acetate	6·1	97–101° C.
Methanol	6·3	64–65° C.
Alcohol 95%, denatured with 2% Toluol	8·3	78° C.
Normal propyl alcohol	11·1	96–98° C.
Butyl acetate, 98/100%	11·8	121–127° C.
Butyl acetate, 85%	12·5	110–132° C.
Monochlor benzene	12·5	130–131° C.
Amyl acetate	13	135–140° C.
Xylol	13·5	137–139° C.
Diethyl carbonate	14	120–130° C.
Isopropyl alcohol	21	79·5–81·5° C.
Isobutyl alcohol	24	104–107° C.
Butanol	33	114–118° C.
Glycol mono-methyl ether	34·5	115–130° C.
Glycol methyl ether acetate	35	138–152° C.
Glycol mono-ethyl ether	43	126–138° C.
Glycol ethyl ether acetate	52	149–160° C.
Dichlorbenzene	57	167–180° C.
Amyl alcohol	62	129° C.
Ethyl butyl carbonate	68	135–175° C.
Cyclohexanyl acetate	77	170–177° C.
Ethyl lactate	80	155° C.
Diacetone alcohol	147	150–165° C.
Butyl glycol	163	164–182° C.
Benzyl acetate	393	213–216° C.
Butyl lactate	443	170–195° C.
Ethyl acetyl glycolate	464	181–195° C.
Benzyl alcohol	1,767	204–208° C.
Glycol	2,625	191–200° C.

the time required for complete evaporation. The time required for the evaporation of ethyl ether is taken as unity, and the figures given for the other solvents represent the time each requires for evaporation compared with that of ethyl ether ; the figures are therefore relative only.[6]

Another authority [7] gives the following :—

Substance.	Evaporation Period.
Ethyl ether	1
Methyl acetate	1·4
Acetone	2·1
Ethyl acetate	5
Methyl ethyl ketone	6·3
Ethyl propionate	9
n-Propylacetate	12
Iso-butyl acetate	15
Butyl acetate 85%	24
Iso-butyl propionate	26
Propyl propionate	39
Amyl forma.e	40
Butyl propionate	60
Amyl acetate	63
Propyl butyrate	73
Ethyl butyrate	80
Isobutyl butyrate	92
Amyl propionate	135
Butyl butyrate	160
Diacetone alcohol	317
Amyl butyrate	443
Cyclohexanyl acetate	491
Methyl cyclohexanyl acetate	554

The agreement with the previous table is obviously not good. Very little reliance however can be placed on most of the published information on evaporation rates, as the phenomenon is profoundly affected by several factors which are difficult to control or standardise. The variations between the results of different investigators are excessively wide.

A critical examination of the known methods for determining evaporation rates has been made by Hofmann,[8] who has determined the rates for several solvents by using a modified form of the apparatus devised by Poleich and Fritz,[9] reasonably consistent results being obtained. These rates are referred to that of butyl acetate, which is taken as 100, and it has been confirmed that approximately accurate results can be calculated from the formula [10] : (vapour pressure × molecular weight) ÷ 11.

The experimental results are given as rates of evaporation at 25° C., viz., :—

$$\frac{\text{time of evaporation of } n\text{-butyl acetate} \times 100}{\text{time of evaporation of other liquid}}$$

the two sets of results are given on p. 42.

Liquid.	Experimental Results.	Calculated Results.
Acetone	850	975
Ethyl acetate	485	582
Alcohol 95%	193	183
Toluene	186	186
sec-Butyl acetate	162	180
sec-Butyl alcohol	110	87·5
n-Butyl acetate	100	100
sec-Amyl acetate	73	85
Xylene	65·5	62
n-Butyl alcohol	45·7	31·7
Glycol mono-ethyl ether	37	37 6

Mixtures.	Composition % by weight at	
	20–25° C.	Boiling Point.
Benzene	46·5	—
Ethyl acetate	53·5	—
Benzene	71·5	60
Methyl alcohol	28·5	40
Carbon tetrachloride	85·5	84
Ethyl alcohol	14·5	16
Carbon tetrachloride	82·5	71
Methyl ethyl ketone	17·5	29
Toluene	46·5	32
Ethyl alcohol	53·5	68
Toluene	50	31
iso-Propyl alcohol	50	69
Toluene	79	—
sec-Butyl alcohol	21	—
Toluene	93	—
sec-Amyl alcohol	7	—
Xylene	66	—
sec-Amyl alcohol	34	—
Xylene	36	—
sec-Butyl alcohol	64	—
Xylene	71	—
n-Butyl alcohol	29	—
Xylene	82	—
Glycol mono-ethyl ether	18	—

The order of this table is in good relative agreement with that given on page 40, where the results are given as evaporation times.

By experimental means, the existence at 20° to 25° C. of a number of constant evaporating mixtures has been established and it is interesting to compare these mixtures with those of constant boiling-point where known. The effect due to the molecular association of the alcohols is shown in the lowering of the proportion of alcohol at the lower temperature. Methyl ethyl ketone also seems to be strongly associated at normal temperatures, and hence evaporates more slowly than would be expected from a consideration of its boiling-point.

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CHAPTER VII

INFLAMMABILITY

THE inflammability of a lacquer is governed initially by the flash-point of its volatile ingredients. Practically all lacquers contain either solvents or diluents of the low-boiling class which flash at ordinary temperatures, *e.g.*, acetone, alcohol, ethyl acetate, benzene, toluene and ligroin.

The flash-point of a mixture of inflammable liquids is not necessarily identical with that of its lowest-flashing constituent —it may be higher or lower. Mixtures of inflammable vapour and air are explosive or inflammable within quite limited ranges of concentration ; a mixture may contain too little or too much of the inflammable vapour for ignition to take place on the application of a flame. The flash-point of a liquid is the temperature at which this minimum concentration is reached.

If to a liquid of given flash-point we add another of higher flash-point, we should, in general, expect the flash-point of the mixture to lie between those of the two liquids taken separately, but it is frequently found that the mixture has a flash-point lower than that of any of its constituents. This phenomenon is caused by the formation of an azeotropic mixture of lower boiling point than those of its constituents. Under such conditions a concentration of vapour sufficiently high to support ignition is reached at a lower temperature than that required by any of the constituents.

The flash-point of a lacquer may be raised in several ways. The first and obvious way is to eliminate wholly or in part those constituents of low flash-point, which generally entails eliminating the " low boilers." A second way is to choose " low boilers " which do not form mixtures of low boiling-point. A third way is to increase the proportion of " high boilers " at the expense of the " medium boilers." Fourthly low-boiling non-associated liquids may be replaced by associated liquids of similar boiling-point, *e.g.*, alcohol for benzene Last and best, a small proportion of highly volatile non-inflammable liquid [1] such as methylene chloride, ethylene

chloride, trichloroethylene, perchloromethane or carbon tetrachloride may be used.

The railway companies classify inflammable liquids in two classes: (1) Those flashing below 73° F. 22·8° C. (closed test); (2) those flashing between 73° and 150° F. 22·8°–65·6° C.; both classes are considered to be dangerously inflammable.

A useful empirical relation has been found, by Ormandy and Craven, between the flash-point of hydrocarbons and the initial boiling-point, viz.: –

$$\text{Flash-point} = (0{\cdot}736 \times \text{boiling-point}) - 72^\circ \text{ C.}$$

This relation is only accurate when the hydrocarbon is free from traces of impurities more volatile than the hydrocarbon itself.

The fire risk attending a lacquer is determined more by its ignition temperature than by its flash-point, *i.e.*, the temperature at which the lacquer will *continue* to burn after ignition; this temperature is generally higher than the flash-point and is determined by the conditions obtaining, viz., a sufficient supply of oxygen; the heat evolved during combustion; the rate at which the heat of combustion is dissipated; and the manner in which the lacquer is disposed; a porous substance, for instance, will act as a wick and promote combustion. The susceptibility of a lacquer to continuous burning can be governed to a slight extent by the inclusion of a substance which leaves a non-inflammable residue on ignition, such as triphenyl phosphate. This device is more effective with the solid film left by a lacquer than with the lacquer itself, but it should be borne in mind that cellulose nitrate is merely a modified form of gun-cotton and contains in itself sufficient oxygen to ensure its complete combustion in a closed space in the absence of air. The only way to extinguish a burning film of cellulose nitrate is to reduce its temperature to below its ignition point; for instance, by flooding with water.

The use of inflammable volatile liquids also involves the risk of explosion, and the conditions under which such explosions may occur have been investigated to a very considerable extent. If the temperature of an inflammable volatile liquid be gradually increased, the air above the liquid becomes progressively richer in inflammable vapour; at a certain concentration the air-vapour mixture can just be

ignited on the application of a flame or spark of sufficient thermal intensity. This concentration, which corresponds with the flash-point, is termed the " lower explosive limit." As the temperature, and hence the concentration, increases, the ease with which the mixture can be ignited also increases and the combustion becomes progressively more violent until a maximum explosivity is reached. On still further increasing the concentration of the vapour the violence of the explosion gradually diminishes until finally the mixture will no longer support combustion, the " upper explosive limit " having been reached.

In the case of hydrocarbons the explosive limits can be correlated with the nature and composition of the liquid.[2] At the upper limit there is twice as much inflammable vapour as there is in a mixture which contains just enough air to correspond with complete combustion ; at the lower limit ignition fails to take place when the mixture contains twice this quantity of air. It appears that these limits are controlled by the amount of heat liberated by the combustion ; the heat of combustion at the limits being just insufficient to maintain the mixture at the ignition temperature.

The upper explosive limit of a substance in a homologous series of which the first terms are known can be calculated from a typical equation. Thus, if n be the number of oxygen atoms required theoretically for the combustion of one molecule of a substance, then for the lower limit the number required is $2n-1$ atoms for a hydrocarbon and $(3n-2)$ for methyl or ethyl alcohol.

The following are considered to be reliable figures [3] :—

Explosive Limits.	Per cent by Volume in Air.	
	Lower Limit.	Upper Limit.
Acetone	2·15	13·0
n-Amyl acetate	1·1	—
n-Amyl alcohol	1·2	—
Amyl chloride	1·4	—
Benzene	1·4	8·0
n-Butyl acetate	1·7	15·0
n-Butyl alcohol	1·7	—
iso-Butyl alcohol	1·68	—
Carbon di-sulphide	1·0	50·0
Cellosolve	2·6	15·7

Explosive Limits.	Per cent by Volume in Air.	
	Lower Limit.	Upper Limit.
Cellosolve acetate	1·71	—
Cyclohexane	1·31	8·35
1.2 Di-chlor ethane	6·2	15·9
1.2 Di-chlor ethylene	9·7	12·8
Di-ethyl ether	1·7	48·0
Ethyl acetate	2·18	11·5
Ethyl alcohol	3·28	19·0
Ethyl formate	3·5	16·5
n-Heptane	1·0	6·0
n-Hexane	1·25	6·9
Methyl acetate	4·1	13·9
Methyl alcohol	5·5	21·0
Methyl *n*-butyl ketone	1·22	8·0
Methyl cyclohexanone	1·15	—
Methyl ethyl ketone	1·81	11·5
Naphtha. V. M. & P.	1·2	6·0
Paraldehyde	1·3	—
n-Propyl acetate	2·0	—
iso-Propyl acetate	2·0	—
n-Propyl alcohol	2·5	—
iso-Propyl alcohol	2·5	—
Toluene	1·27	7·0
Turpentine	0·8	—
o-Xylene	1·0	5·3

The temperature of the air-vapour mixture affects the explosive limits, increase in temperature causing an increase in the range.[4]

Temperature.	Lower Limit.	Upper Limit.
50° C.	1·5	4·85
300° C.	1·3	6·2

The figures refer to toluene-air mixtures, ignited by an electric spark in a glass apparatus.

Large changes in pressure also affect the limits.[5]

Le Chatelier [6] found that for a mixture of substances whose lower limits taken separately contain N_1, N_2, N_3, etc.,

percentage of each substance in air, the composition of the lower limit mixture is given by

$$n_1/N_1 + n_2/N_2 + n_3/N_3 + \ldots = 1,$$

where n_1, n_2, n_3, etc., are the percentages of the different substances in the mixture.

Richardson and Sutton [7] have investigated experimentally the explosive properties of the vapours of certain lacquer solvents at normal temperatures under conditions which approximate to those obtaining in "spray booths." They point out that in order that an explosion may occur sufficient heat must be liberated by the burning vapour to heat the adjacent layers to their ignition temperature, and that the thermal conductivity of the vapour must be high enough to permit this necessary flow of heat; when the amount of the solvent vapour in the air is low, the thermal conductivity of the mixture is nearly the same as that of air, and the heat of combustion is the chief factor governing the explosion under these conditions, *i.e.*, at the lower explosive limit; the higher the heat of combustion the greater the explosivity.

The following are the heats of combustion in calories per gram of some volatile liquids in common use :—

Heptane	11,375	Ethyl ether	8,807
Hexane	10,636	Acetone	7,304
Paraffin	10,340	Alcohol	7,080
Toluene	10,150	Ethyl acetate	6,103
Benzene	9,960	Methyl alcohol	5,331

At first sight it appears anomalous to state that heptane has a higher explosivity than ether, but a necessary condition is that the proportion of the vapour in the air is sufficiently high. It follows, given the necessary conditions, that mixtures of heptane and air explode with greater violence than corresponding mixtures of ether and air.

It will be noticed that the heats of combustion for alcohols and esters are, in general, much lower than those of hydrocarbons; a greater concentration of the former is, therefore, necesssary if an explosive mixture is to be formed.

Liquids having boiling-points above about 113° C. do not form explosive mixtures with air at 25°, since a sufficiently high concentration of the vapour cannot be obtained. A point of practical interest is that concentrations which can be inhaled

Auto-ignition Temperatures

	°F.	°C.
Acetone	1118	604
n-Amyl acetate	714	379
iso-Amyl acetate	715	379
n-Amyl alcohol	621	327
iso-Amyl alcohol	667	353
Benzene	1076	580
Benzyl acetate	862	461
Benzyl alcohol	817	436
n-Butyl acetate	790	421
n-Butyl alcohol	693	367
iso-Butyl alcohol	825	441
tertiary Butyl alcohol	901	483
Butyl carbitol	442	228
Butyl cellosolve	472	244
n-Butyl proprionate	800	427
Camphor	871	466
Carbon di-sulphide	257	125
Castor oil	840	449
Cellosolve	460	238
Cellosolve acetate	715	379
Cymene	921	494
Decahydronaphthalene	504	262
syn-Di-chlor ethyl ether	696	369
Di-ethylene glycol	444	229
Ether	366	186
Ethyl acetate	907	486
Ethyl alcohol	799	426
1.2 Di-chlor ethane	775	413
Ethylene glycol	775	413
n-Heptane	452	233
n-Hexane	477	247
Methyl acetate	935	502
Methyl alcohol	887	475
Methyl cellosolve	551	288
Methylene chloride	1224	662
iso-Propyl acetate	860	460
n-Propyl alcohol	812	433
iso-Propyl alcohol	852	456
iso-Propyl ether	830	443
Toluene	1026	552
Turpentine	488	253
Xylene	920	493

without producing pronounced narcotic effects are non-explosive, but in any given space the possibility of the existence

of local concentrations above the lower explosive limit should not be overlooked.

A mixture of inflammable vapour and air may ignite without the actual application of a flame or a spark, provided its temperature be sufficiently high ; this temperature is termed the self- or auto-ignition temperature.

Thompson [8] determined the auto-ignition temperatures of a number of lacquer solvents. His results are, however, profoundly affected by the material of which the apparatus for determining the temperatures is constructed, and must be taken with due reserve.

There seems to be no periodic relationship connecting the auto-ignition temperature and specific gravity, vapour pressure, heat of combustion, oxygen content or size of the molecule.[9]

References

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CHAPTER VIII

TOXICITY

IT is safe to say that the vapours of all volatile substances are toxic, in the widest sense, if they be inhaled in a sufficiently concentrated state for a sufficient length of time. The effects are termed acute or chronic, according to the degree and permanence of the resulting toxæmia. Acute poisoning is usually the result of relatively short exposures to high concentrations ; chronic poisoning, while it can be caused by similar conditions, is more usually the result of prolonged exposure to relatively low concentrations. Acute poisoning, if not quickly fatal, is usually the less dangerous and more easily remedied than the more profound damage of chronic poisoning ; moreover, acute poisoning is more dramatic in its effects and much more easily perceived than the slow deterioration of bodily health accompanying chronic poisoning. There is obviously no hard and fast division of the two types, but the terms afford a convenient distinction.

One of the most important factors governing toxicity is the volatility of the solvent, since this largely governs the concentration which can arise under given conditions. Air can carry a greater quantity of a highly volatile solvent in a state of vapour at ordinary temperatures than it can of one of low volatility ; the probability of a lethal concentration being reached is, therefore, greater with the low-boiling solvents than with the high-boiling ; this factor to a large extent eliminates the very high-boiling solvents and plasticisers from consideration, but not entirely since entry to the system can occur through the mouth or by absorption through the skin, poisoning has occurred in the former way by tricresylphosphate causing paralysis.

Unfortunate and unexpected catastrophies which occurred about the year 1933 showed the necessity for a comprehensive examination of the position, and this task has been undertaken by authorities in collaboration with the Home Office. It has been thought advisable to attempt to give some guidance so

far as published information permits; the aspect of the problem dealt with here being mainly that of the inhalation of air charged with the vapour of the solvent at ordinary atmospheric temperatures.

Benzene

Benzene (benzol) produces very severe toxic effects; at high concentrations it has a severe irritant and destructive action on the central nervous system, producing convulsive movements followed by paralysis, unconsciousness with dilated and unreactive pupils and in severe cases death. At lower concentrations, benzene causes giddiness, headache, nausea, a sensation of tightness of the chest and an inability to escape from the site of the poison. Prolonged contact at quite low concentrations causes loss of appetite and damage to the blood-forming organs.

The maximum permissible concentration for prolonged contact is estimated to be 100 p.p.m.; a concentration of 3,000 p.p.m. is dangerous for exposures exceeding half an hour, while 20,000 p.p.m. quickly produces fatal results.

Toluene

Toluene appears to have an acute narcotic effect similar to that of benzene. In high concentrations it is considered to be more dangerous to life than benzene, but to be less active in causing chronic poisoning by prolonged contact. Agreement is fairly general that toluene in actual use under industrial conditions is less dangerous than benzene, probably on account of its lower volatility.

Xylene

Uncertainty exists regarding the precise degree of the toxicity of xylene, but it appears to be less dangerous than benzene. No fatal case of poisoning due to the inhalation of xylene has been recorded. High concentrations cause giddiness, intoxication and loss of consciousness. Prolonged contact causes symptoms similar to those caused by toluene, accompanied by injury to the kidneys, heart and arteries.

In industrial processes the concentration of xylene in the air is not likely to exceed 10,000 p.p.m., which concentration is probably non-fatal for short periods of contact; the fatal

concentration for short exposure is estimated to be 19,000 p.p.m.

Coal Tar Solvent Naphtha

There are no recorded fatalities caused by coal tar solvent naphtha. Severe exposure induces acute poisoning leading to giddiness, intoxication, irregular breathing and unconsciousness. Chronic poisoning is shown by derangement of the nervous and digestive systems.

Petroleum Spirit

The toxicity of petroleum fractions varies considerably with the composition ; as a rough guide, it may be taken that the toxicity of a petroleum fraction having a volatility similar to that of benzol is about one-half that of benzol ; the acutely toxic effects of petroleum is attributed mainly to the cyclo-paraffins, but the poisoning, whether acute or chronic, is essentially one of nerve poisoning. Prolonged contact may give rise to anæmia, loss of weight and general disturbance of health.

Acute poisoning induced by high concentrations may lead to fatal results preceded by loss of consciousness, irregular respiration, convulsions and heart failure; the fatal concentration for short exposure to gasoline is estimated to be 24,300 p.p.m.

White Spirit

The low volatility of this solvent precludes the possibility of dangerously narcotic concentrations being reached under conditions of normal usage. The vapour causes giddiness, mild intoxication and vomiting, but recovery from the effects of short periods of contact is rapid and there appear to be no residual symptoms. Prolonged contact may cause temporary deafness.

Turpentine

The question of the occurrence of chronic poisoning by the inhalation of turpentine vapours is not definitely settled, but it is generally considered that prolonged contact with low concentrations is comparatively harmless. Exposure to high concentrations causes giddiness, drowsiness, nausea and colic, but the symptoms are of short duration. High concentration

may cause irritation of the skin and mucous membranes; 4 mg. per litre causes smarting of the eyes.

Cyclohexane

High concentrations cause staggering and paralysis. The lethal concentration has been said to be 600 mg. per litre.

Chronic effects due to prolonged contact with low concentrations appear to be similar to those of benzene, but very much less severe.

Tetrahydronaphthalene

This material appears to be relatively innocuous; the inhalation of the vapour causes headache, nausea and slight stupor, irritation of the mucous membrane and some derangement of the kidneys.

Carbon Disulphide

Carbon disulphide is dangerously narcotic at high concentrations, and may cause failure of the respiration. Concentrations over 400 p.p.m. must be considered dangerous, but there is considerable variation in individual susceptibility.

It is a severe chronic general nerve poison and produces conditions varying from slight fatigue, giddiness, pain in head and limbs, disturbed vision and digestion, hysteria to complete paralysis.

Methyl Alcohol

It seems well established that methyl alcohol is a poison and will produce dangerous results if a sufficient amount is taken into the body. Toxic effects can be produced by absorption through the skin as well as through the lungs. It is considered that the hazard involved by absorption through the skin is not great for humans, but it should be borne in mind that methyl alcohol is cumulative in the body and is oxidised slowly therein to formaldehyde and formic acid.

Exposure to high concentrations of vapour causes giddiness, unconsciousness, slowing of the heart, cold sweats and in severe cases death; prolonged exposure to lower concentrations causes acute derangement of the digestive system and eyes, even resulting in sudden and permanent blindness.

It is considered that a concentration of 1,000 p.p.m. is the threshold of toxicity, and one of 100 p.p.m. should never be exceeded in the air of workshops.

Ethyl Alcohol

Ethyl alcohol is more acutely toxic than methyl alcohol, but its effects are much more transient as it is oxidised in the system to carbon dioxide and water. Intoxication by the inhalation of the vapour is not likely to occur under industrial conditions with concentrations less than 1,000 p.p.m. Stupor and drowsiness are slowly induced by a concentration of 5,000 p.p.m. Acute intoxication may follow with repeated application of alcohol to the skin.

Propyl Alcohols

The propyl alcohols seem to offer little risk ; the narcotic dose is stated to be about one-third and the lethal dose about one-half that of ethyl alcohol. These do not appear to be absorbed to any dangerous extent by the skin.

Butyl Alcohols

Prolonged exposure is said to produce anæmia, very few ill effects can be attributed to repeated exposure to non-narcotic concentrations. Secondary butyl alcohol is probably slightly more toxic than *n*-butyl alcohol.

Amyl Alcohols

Fused oil amyl alcohols are apparently innocuous at low concentrations, causing little more than irritation of the throat ; high concentrations cause headache, giddiness, nausea, and prolonged contact at high concentrations causes diarrhœa, deranged vision and delirium.

Cellosolve (Ethyl Glycol)

Prolonged exposure may cause some slight degree of damage to the liver and kidneys, but otherwise the substance appears to be relatively harmless.

Cyclohexanol and Methyl Cyclohexanol

The low volatility of these alcohols precludes any serious danger from inhalation of air mixtures. They tend to cause nausea and have some slight action on the blood, but otherwise they appear to be non-toxic.

Ethyl Ether

Is a powerful narcotic, concentrations of 35,000 p.p.m. can produce unconsciousness, but with normal constitutions

neither acute nor chronic intoxication appear to be accompanied with any serious or lasting effects, provided a lethal concentration is not reached. The high volatility of ether makes such a possibility not improbable.

Dioxane

Dioxane possesses insidious long-range effects, and has been the cause of several fatalities. Prolonged exposure may cause lesions of the kidneys and liver, and other severe toxic effects. Toxic amounts can be absorbed through the skin. The symptoms of dioxane poisoning include irritation of the nose and eyes, drowsiness, vertigo, headache, loss of appetite, tenderness in abdomen, and a feeling of chilliness. The provisions of section 43 of the Workmen's Compensation Act, 1925, apply to disease and injury caused by dioxane.

Ethyl Formate

Probably less toxic than butyl and amyl formate, but more so than the acetate. It has an irritating action on the mucous membranes and a paralytic action on the nervous system.

Butyl Formate

Comparatively short exposure to concentrations of 10,000 p.p.m. is intolerable both as regards breathing and sight.

Amyl Formate

The narcotic potency of amyl formate is said to be about three times as great as that of amyl acetate.

Methyl Acetate

A concentration of 10,000 p.p.m. causes irritation of the eyes, nose and throat, followed by headache and drowsiness.

Ethyl Acetate

Ethyl acetate has but a low order of toxicity, chronic effects appear to be limited to irritation of the mucous membrane and a tendency to eczema. High concentrations have a narcotic effect.

Propyl Acetates

These esters are somewhat more irritating to the mucous membrane than ethyl acetate and the narcotic potency is considerably higher.

N-Butyl Acetate

Regarded as one of the least toxic of all organic solvents ; mild narcosis is produced by 5,000 p.p.m. Contact over long periods causes depression, exhaustion and loss of weight.

Amyl Acetate

When inhaled in high concentrations, amyl acetate has the irritative and narcotic action common to esters of this class.

Workers exposed for long periods experience irritation of the mucous membrane, but only slight disturbances to general health, such as headache, loss of appetite and loss of weight. Immunity is, however, generally established quite rapidly.

The minimum narcotic concentration for prolonged exposure is about 4,000 p.p.m. ; the secondary effects of narcosis are slight, and recovery is rapid with no constitutional disturbances. The narcotic effect is said to be lower than that of butyl acetate.

Benzyl Acetate

Benzyl acetate is more irritating and narcotic than the aliphatic acetates. The narcotic effect is rarely observed with air mixtures obtained by evaporation, but when the ester is sprayed the irritative effect may be marked.

Acetone

The narcotic action is more rapid than that of methyl alcohol, but the toxicity much less.

Concentrations up to 40,000 p.p.m. cannot be inhaled for more than a few minutes owing to acute irritation of the throat and eyes. It is estimated that about 75% of the inhaled acetone is absorbed by the system. Prolonged exposure to low concentrations does not seem to cause dangerous results.

Methyl Ethyl Ketone

Irritation to eyes and throat is caused by concentrations of 3,000 p.p.m. ; concentrations of 10,000 p.p.m. are intolerable.

Mesityl Oxide

The maximum supportable concentration of this substance is considered to be ·24% in air but its odour and irritant properties do not constitute an adequate warning of its presence. Little is known of its toxic properties.

Ethylene Chlorhydrine

Inhalation causes severe nerve and metabolic poisoning with irritation of the mucous membrane and lungs, which may end fatally ; early symptoms are nausea, drowsiness, headache, stupor and vomiting of a yellow fluid. Chronic effects may be produced by absorption through the skin.

Methylene Dichloride

Methylene dichloride is less narcotic than chloroform, but more irritating to the respiratory passages. High concentrations cause severe headache, pains in limbs, acceleration of the heart and difficulty in breathing. Owing to its high volatility, narcotic concentrations may be easily reached.

Chloroform

High concentrations rapidly produce insensibility and death ; 25,000 p.p.m. produces death in 5 to 10 minutes ; 15,000 p.p.m. can be tolerated for about half an hour and 5,000 p.p.m. for periods exceeding one hour. Concentrations exceeding about 750 p.p.m. are considered dangerous. Prolonged contact at low concentrations give rise to symptoms resembling those of chronic alcoholism.

Carbon Tetrachloride

Immediate death due to acute narcotic poisoning is comparatively rare, but acute symptoms may follow some days after. Acute poisoning occurs with concentrations of 1,000 p.p.m., while chronic effects may result from prolonged exposure to 100 p.p.m. The odour of carbon tetrachloride can be detected with 80 p.p.m., while one half an hour's exposure to 300 p.p.m. may cause intoxication. Chronic poisoning is characterised by loss of weight and appetite, jaundice, disturbance of vision, mental confusion and injury to liver and kidneys.

Dichlorethane

This is a powerful narcotic similar to chloroform in its action, concentrations of 6,000 p.p.m. are considered to be dangerous. It causes vomiting, diarrhœa and giddiness but there is little evidence of any cumulative effect.

Tetrachlorethane

Considered to be the most dangerously toxic substance of the chlorinated hydrocarbon class, it exerts not only a

powerful narcotic effect, but produces profound metabolic injury, especially enlargement of the liver. Diseases caused by contact with this substance are notifiable under the Factory and Workshop Act, section 73, Order No. 1170 of November, 1915.

Its narcotic toxicity is about four times that of chloroform, but recovery from anæsthesia is more regular.

Its chronic effects are jaundice, toxæmia, damage to the internal organs, particularly the liver, the symptoms being abnormal fatigue, nervousness, loss of appetite, nausea and vomiting.

Fatal concentration for short exposure 7,300 p.p.m.

Pentachlorethane

Pentachlorethane is a narcotic poison of considerable potency and produces toxic effects similar to those of tetrachlorethane.

Fatal concentration for short exposure 9,600 p.p.m.

Trichlorethylene

This substance does not seem to cause damage to the liver and kidneys, but it is a narcotic of considerable potency. Many cases have been reported of acute narcosis ending fatally, following exposure to high concentrations which can easily be reached by reason of the high volatility of the substance. Trichlorethylene is somewhat more toxic than chloroform.

Fatal concentration for short exposure 37,000 p.p.m. There is little evidence of any cumulative effect.

Perchlorethylene

Perchlorethylene is less narcotic than chloroform or carbon tetrachloride, but it has a toxic action on the liver and kidneys. It is usually considered to be the least toxic of industrial aliphatic chloro hydrocarbons.

Fatal concentration for short exposure 30,900 p.p.m.

Monochlorobenzene

Monochlorobenzene is a narcotic of considerable potency-producing effects like those of benzene, but probably less severe.

Dichloroethylether

This substance produces acute irritation of the mucous membrane. A concentration of 1,000 p.p.m. is intolerable,

and one of 500 p.p.m. causes irritation of the eyes, nose and lungs.

An attempt has been made to classify the various solvents into three classes, according to the relative degree of danger which they probably present under factory conditions, but it should be borne in mind that the only positively safe course is to prevent contact with the solvent.

Solvents of Low Toxicity

White spirit, tetrahydronaphthalene, turpentine, ethyl alcohol, propyl alcohols, butyl alcohols, amyl alcohols, ethyl glycol, cyclohexanol, methylcyclohexanol, acetone, ethyl acetate, propyl acetate, butyl acetates, amyl acetates, plasticisers.

Dangerously Toxic Solvents

Benzene, toluene, cyclohexane, carbon disulphide, methyl alcohol, dioxane, methylene dichloride, chloroform, carbon tetrachloride, dichlorethane, tetrachlorethane, pentachlorethane, trichlorethylene, dichlorethyl ether, chlorobenzene, ethylene chlorhydrine.

The toxicity of solvents not included in the above classes are either insufficiently known or moderately high.

Methods for the detection of certain solvents have been published by the Department of Scientific and Industrial Research, H.M. Stationery Office, W.2.

Other books which should be consulted are :—

" Toxicity of Industrial Solvents," by E. Browning, H.M. Stationery Office, and " Toxikologie und Hygiene der technischen Losüngsmittel," by K. B. Lehmann and F. Flury.

PART II

INTRODUCTION

THE figures quoted in this section for the physical and chemical characteristics of a solvent refer primarily to those obtaining for a technical product of good quality. It should be borne in mind that the products emanating from different sources may vary in their purity, and the figures given should in general be regarded as the permissible limits rather than those usually occurring. The figures relating to the characteristics of the pure substance frequently follow those of the technical product in order that some idea can be obtained regarding the purity of the latter. It should be borne in mind that the quality or composition of a solvent may be varied to suit trade conditions, but the trend is generally towards greater purity.

In many cases it is not desirable or expedient that a chemically-pure substance should be used for lacquers. In some instances the presence of " impurities " considerably enhances the desirable properties of a solvent. On the other hand, the cost of removing certain impurities may be out of proportion to the advantages to be gained.

Specifications of an official nature which are quoted are not given verbatim, but in a convenient abbreviated form suitable for quick reference only ; if more definite details are desired, the original specifications should be consulted.[1]

The endeavour has been made to make this section as complete as possible, and every source of information available has been freely made use of ; it has not always been feasible to make adequate acknowledgment. The author has also drawn largely from his own experience, and is greatly indebted to Messrs. A. Boake Roberts & Co., Ltd., for permission to use the information gained in their laboratories. He would like to acknowledge the assistance afforded by many firms, both in this country and in America, France and Germany.

It has not been possible for the author personally to verify all the information collected here, and it is therefore likely

that inaccuracies will be found; he would welcome any correctional or supplementary information. It has been difficult on occasion accurately to modify the somewhat extravagant claims not infrequently made for specific solvents, and to bring conflicting views into accordance.

The proprietary names which are quoted are in many instances trade marks. The composition of the articles to which these names refer is generally that quoted in various journals or catalogues, and is given in all good faith, but without any guarantee of accuracy.[2]

In view of the very large and increasing number of these proprietary names, they have mostly been eliminated from the text and can be found in Appendix I. It has also been thought advisable to remove from the text most of the statements regarding toxicity and to deal more comprehensively with this aspect in Chapter VIII.

References

[1] B.E.S.A. and British Standard Specifications are abstracted by permission of the British Standards Institution, 28 Victoria Street, London, S.W.1, from whom official copies of the full specifications can be obtained.

A.S.T.M. Specifications are abstracted by permission of the American Society for Testing Materials, 260 South Broad Street, Philadelphia.

[2] *Cf.* VAN HOCK. *Farb. Zg.*, 1927, **32**, No. 31, p. 1737; NOLL, *ibid.*, 1927, April, pp. 1553 *et seq.* *Farbe und Lac.*, 1926, **31**, pp. 6, 92, 172. *Enduits Cellulosiques*, W. Main, 1930, Paris. *Losüngsmittel*, O. Jordan, 1932, Berlin. *Celluloseester Lacke*, Bianchi-Weihe, 1931, Berlin. *Decknamen u. chem. Zusammensetzung*, H. Ulrich, 1935, Hamburg. *Technologie d. Weichmachungsmittel*, W. Munziger, 1935, Munchen. *Losüngsmittel u. Weichmachungs Mittel*, Durrans-Merz, 1933, Halle. "Physical and Chemical Examination of Paints, etc.," Gardner, Washington.

ABBREVIATIONS

S.G.	Specific gravity at 15·5° C. (60° F.), unless otherwise stated.
B.R.	Boiling-range in deg. C. of commercial products.
B.P.	Boiling-point in deg. C. of pure substance.
V.P.	Vapour pressure in millimetres of mercury of pure substance at 20° C.
F.P.	Flash-point.
I.P.	Permanent ignition-point.
S.P.	Solidifying-point in deg. C.
M.P.	Melting-point in deg. C.
R.I.	Refractive index at 20° C. for D line.
L.H.	Latent heat of vaporisation in gram calories per gram.
S.H.	Specific heat, gram cals per gram.
E.R.	Evaporation rate (ether = 1).
K.B.V.	Kauri-butanol value.
A.P.	Aniline point ° C.
H.C.	Heat of combustion in gram calories per gram.
Dil. Rat.	Dilution ratio for nitrocellulose.
Cub. Exp.	Co-efficient of cubical expansion, per 1° C. at about 20° C.
Vis.	Viscosity in centipoises at 20° C.
S. Ten.	Surface tension in dynes per c.m. at 20° C.
Elec. Cond.	Electrical conductivity in reciprocal ohms at 25° C.
Dielec. Const.	Dielectric constant at ∞ frequency at 20° C.
Crit. Temp.	Critical temperature.
Exp. Lim.	Explosive limits in percentages by volume in air.

Binary mixtures are given in percentages by weight.

CHAPTER I

HYDROCARBONS AND SUNDRY SOLVENTS

Benzene. C_6H_6

BENZENE, known commercially as benzol, is a coal-tar product, and is not to be confused with benzine, which is a petroleum distillate consisting mainly of hexane and heptane (*vide* petroleum hydrocarbons).

Benzene is largely used as a diluent for lacquers, but its toxic and narcotic nature militate against its use except under conditions of adequate ventilation. Commercial benzene may contain traces of toluene, xylene, carbon disulphide, thiophene, acetonitrile and pyridine. It is a solvent for a number of cellulose esters and ethers, in particular ethyl cellulose ; cellulose dinaphthenate ; dilaurate ; dipalmitate ; distearate ; dinitrolaurate ; dinitropalmitate ; diacetyl laurate and diacetyl palmitate.[1] If mixed with alcohol, it will dissolve benzyl cellulose and other ethers. It is a solvent for most oils, and for ester gum, benzylabietate, copal ester, polystyrene, cumarone, benzyl resin, mastic, plextol, cyclohexane resins ; Albertols 82G ; 111L ; 209L ; raw rubber ; gutta percha resin ; thio-urea resins ; chlornaphthalene resin and naphthalene formaldehyde resin. It does not dissolve cellulose acetate or nitrate, copal or shellac, and is non-miscible with water, aqueous solvents and glycols, monochlorhydrine, monacetin. Cellulose acetate absorbs 22% by weight of benzene at 25° C. Benzene is available in several grades, as follows :

British Standard Pure Benzole [2] 135*A*—1939.

S.G. ·880–·885 (·874–·879 at 20° C.) B.R. 90% over 0·5° C. between the limits 79·5° and 80·5° C. Residue ·01% max. Neutral, Sulphur ·2% max.

British Standard Industrial Benzole 135*E*—1939.

S.G. ·870–·885 (·864–·879 at 20° C.). B.R. up to 100° C. 65% min. up to 120° C. 85% min. Up to 145° C. 95·% min. Residue ·01% max. Sulphur ·4% max.

British Standard 90's *Benzole* 135*D*—1939.

S.G. ·877–·884 (·871–·878 at 20° C.). B.R. 90% min. up to 100° C.; 97% min. up to 115° C. Residue ·01% max. neutral. Sulphur ·4% max.

A.S.T.M. 90% *Benzene D*361–36.[3]

S.G. ·868–·882 at 20°. B.R. below 77° none. 100°–92% min. above 122° none. Residue ·005% max. Acidity, none. Sulphur none.

Commercial Crystallisable 100% *Benzene.*

S.G. ·882. B.R. 80°–81°. Residue 0·01% max.

Commercial 90's *Benzol.*

90% by volume distils below 100° C. F.P. — 5° F. (—21° C.). R.I. at 25° about 1·497.

Chemically-pure Benzene.

S.G. at 20°, ·8791. M.P. 5·5° C. B.P. 80·1° C. V.P. 75. F.P. —11° C. (12° F.). R.I. 1·501. S.H. ·408. L.H. 94. Elec. cond. 5×10^{-17}. Dielec. const. 2·3. Vis. 66. K.B.V. 100. Cub. exp. ·00124.

The following azeotropic mixtures are known:

Benzene 55%	Cyclohexane	45%	B.P. 77·8°
,, 19%	*n*-Hexane	81%	,, 68·9°
,, 60%	Methyl alcohol	40%	,, 58·3°
,, 68%	Ethyl alcohol	32%	,, 68·2°
,, 83%	*n*-Propyl alcohol	17%	,, 77·1°
,, 67%	*iso*-Propyl alcohol	33%	,, 71·9°
,, 91%	*iso*-Butyl alcohol	9%	,, 79·8°
,, 62%	Methyl ethyl ketone	38%	,, 78·3°

Benzene dissolves 0·24% by weight of water at 22° C.
Water dissolves 0·07% by weight of benzene at 22° C.

Toluene. $C_6H_5 . CH_3$

Toluene or toluol is the most widely-used hydrocarbon "diluent" in lacquers, its vapour pressure and power of dissolving resins making it very suitable for this purpose. Its odour is somewhat objectionable; it is narcotic, but not

dangerously toxic, being much superior to benzene in this respect.

It is not a solvent for cellulose esters, but solutions of these in most of the solvents will usually tolerate the addition of a greater proportion of toluene than of any other hydrocarbon diluent. Cellulose acetate absorbs 17% by weight of toluene at 25° C.

Toluene is a solvent for ethyl cellulose, ester gum, copal ester, benzyl abietate, polystyrene, cumarone, cyclohexane-formaldehyde resin, Albertols 82G; 111L; 209L; raw rubber; gutta percha resin; and mastic, but not for copals or shellac. It gelatinises di-benzyl cellulose. It is miscible with castor, linseed and other oils, and with hydrocarbons and solvents, but not with industrial alcohol (except in limited ratios), monochlorhydrine, monacetin, glycol, or water.

Characteristics of Pure Toluene: S.G. ·871. B.P. 110·6. M.P. −95° C. V.P. 22. F.P. 40° F. (4° C.). I.P. about 70° F. (21° C.). R.I. 1·499. L.H. 86. S.H. ·392. Vis. ·58. Cub. exp. ·00107. S. ten. 30 at 80° F. Elec. cond. $1{\cdot}4 \times 10^{-14}$. Dielec. const. 2·38.

A.S.T.M. Industrial Pure Toluene, *D*362-36[3] has: S.G. ·860–·870 at 20°. B.R. below 107·5°, none; above 112·5°, none. Total boiling range 3·0°. Residue ·005% max. Acidity, none. Sulphur, none.

British Standard Pure Toluole [2] 805A—1939.

S.G. ·867–·872 (·862–·867 at 20°). B.R. 90% min. over 1° range between 107·5 and 111·5° C. Residue ·01% max. Sulphur ·2% max. Neutral.

British Standard 90's Toluole [2] 805C—1939.

S.G. ·860–·875 (·855–·870 at 20° C.). B.R. up to 101°—5% max.; up to 120°—90% min. Residue ·01% max. Sulphur ·2% max. Neutral.

British Standard 95's Toluole [2] 805D—1939.

S.G. ·866–·872 (·861–·867 at 20° C.). B.R. up to 107·5°—5% max.; up to 120°—95·% min. Residue ·01% max. Sulphur ·1% max. Neutral.

The rate of evaporation of toluene is about four times that of *n*-butyl alcohol and about twice that of butyl acetate. Water dissolves 0·047% of toluene at 20° C.

The following azeotropic mixtures are known :—

Toluene 32%.	Ethyl alcohol 68%.	B.P. 76·7°
„ 51%.	*n*-Propyl alcohol 49%.	„ 92·6°
„ 31%.	*iso*-Propyl alcohol 69%.	„ 80·6°
„ 68%.	*n*-Butyl alcohol 32%.	„ 105·5°
„ 56%.	*iso*-Butyl alcohol 44%.	„ 101·1°
„ 74%.	Epichlorhydrine 26%.	„ 108·3°

and a ternary mixture consisting of toluene 50%, ethyl alcohol 38%, water 12%, boiling at 74·6° C.[15]

Xylene. $CH_3 . C_6H_4 . CH_3$

Commercial xylene or xylol consists of a mixture of the three isomeric xylenes in which *meta*xylene usually preponderates. The boiling-points of the three isomers are very close together, being for *ortho*xylene 142–3°, *meta*xylene 139°, and *para*xylene 138°. Commercial xylene also usually contains small quantities of toluene, ethyl benzene, and of the three tri-methyl benzenes, in particular the 1 . 3 . 4 tri-methyl benzene or pseudocumene. It is immaterial, for solvent purposes, which of the three xylenes preponderates, but the presence of toluene lowers the flash-point and the tri-methyl benzenes lower the rate of evaporation. Xylene has an evaporation rate about the same as that of amyl acetate.

Xylene is not normally a solvent for cellulose esters, but in the presence of anhydrous alcohol it dissolves some forms of the nitrate. Cellulose acetate absorbs 5% by weight of *m*-xylene at 25° C.

Xylene is a solvent for dibenzyl cellulose, ester gum, copal ester, benzyl abietate, rubber, gutta percha resin, polystyrene, castor, linseed and other oils. It is miscible in all proportions with petroleum hydrocarbons, and with practically all of the cellulose ester solvents with the exception of diacetin, monochlorhydrine, glycols and industrial alcohol. It forms constant-boiling mixtures with iso-amyl alcohol, iso-amyl acetate, methyl lactate.

Xylene has a narcotic effect if inhaled in a concentrated state, but is not dangerously toxic.

British Standard 2° *Xylole* [2] 458*A*—1939.

S.G. ·865–·870 (·860–·865 at 20° C.). B.R. 92% min. over 2° range between 138° and 142° C. Residue ·01% max. Neutral. Non-sulphonable hydrocarbons 4% max. Flash point 75° F. min.

British Standard 3° *Xylole* [2] 458*B*—1939.

S.G. ·858–·870 (·853–·865 at 20° C.). B.R. 90% min. over 3° range between 138° and 144° C. Residue ·01% max. Neutral. Flash-point 75° F. min.

British Standard 5° *Xylole* [2] 458*C*—1939.

S.G. ·855–·870 (·850–·865 at 20° C.). B.R. 90% min. over 5° range between 135° and 145° C. Residue ·01% max. Neutral. Flash-point 75° F. min.

A purified xylene of high flash-point is also available: B.R. 138°–140° C. F.P. about 85° F. (30° C.). I.P. about 116° F. (46°C.). Vis. about ·65. L.H. 82. S.H. ·4. Auto-ignition temperature 136° C. K.B.V. 85–90. Cub. exp. ·001.

*A.S.T.M. Industrial Xylene or Solvent Naphtha D*364–36 [3] has: S.G. ·856–·867 at 20°. B.R. up to 123°, none; 129° 5% max.; 143° 90% min.; above 160°, none. Residue ·005% max. Acidity, none. Sulphur, none.

The following azeotropic mixtures are known :—

o-Xylene 40%.	Iso-amyl alcohol 60%.	B.P. 128·0°
m- ,, 47%.	,, 53%.	,, 127·0°
m- ,, 46%.	Iso-amyl acetate 54%.	,, 136·0°
p- ,, 49%.	Iso-amyl alcohol 51%.	,, 126·8°

Coal-tar Solvent Naphtha

Coal-tar solvent naphthas are mixtures of aromatic hydrocarbons together with small proportions of naphthenes and paraffin hydrocarbons; the chief ingredients are toluene, xylene, ethyl benzene, propyl benzenes, pseudocumene, mesitylene, ethyl xylene, hemimellithene, durene, indene and cumarone. In general they are not suitable for use in cellulose lacquers but they are solvents for ester gum, ethyl and benzyl abietates, bitumen, pitches, many resins and oils.

There are three recognised qualities for rectified material as follows :—

British Standard Coal Tar Solvent Naphtha (96–160) [2] 479A —1939.

S.G ·854 min. B.R. up to 125° C. 5% max.; up to 160° 96% min. Residue ·01% max. Neutral.

British Standard Coal Tar Solvent Naphtha (90–160)[2] 479*B*—1939.

S.G. ·850 min. B.R. up to 125° C. 5% max.; up to 160° 90% min. Residue ·01% max. Neutral.

British Standard Coal Tar Heavy Naphtha (90–190)[2] 479*C*—1939.

S.G. ·860 min. B.R. up to 160° C. 5% max.; up to 190° 90% min. Flash-point 90° F. min. Phenols ·25% max. Pyridine ·25% max. Naphthalene—special test.

Cymene. *p.* $CH_3 . C_6H_4 . CH\begin{matrix}CH_3\\CH_3\end{matrix}$

Cymene, cymol or *p.* methylisopropylbenzene has been suggested as a high-boiling diluent for lacquers.[4] It is a pleasant-smelling liquid, having an odour like that of parsley. It occurs in light resin oil and in spruce turpentine; it is obtained as a by-product in the manufacture of sulphite paper pulp, probably resulting from the dehydrogenation of pinene by sulphur.[5]

Its physical characteristics vary with its source. Sulphite-pulp cymene has S.G. ·857 at 20°. R.I. 1·49. B.P. 174–177. Cymene from other sources has S.G. ·859–·864. B.P. 175–177·3. M.P. —73·5. Vis. 1 at 25°. R.I. 1·49. F.P. 100° C. (212° F.). It forms a constant-boiling mixture with 71% of cyclohexanol boiling at 159°.

It is an excellent solvent for many resins, but not for cellulose esters. It is miscible with oils and hydrocarbons and most of the usual solvents, but not with water. It is a stable substance and does not readily oxidise in the air, and finds use as a substitute for turpentine.

Dipentene. $C_{10}H_{16}$

Dipentene is a terpene which occurs widely in volatile essential oils. It is a colourless liquid having a faint lemon odour, the pure substance has S.G. at 20° ·844. R.I. 1·472. B.P. 175°–176°. A technical product is available [6] having S.G. ·845–·860. F.P. 130° F. (43° C.). R.I. 1·472–1·477. B.R. 170°–188° (90%, 177°–182°). K.B.V. 105. Products containing high percentages of dipentene together with similar terpene hydrocarbons are also available. "Solvenol" or

" Terpentinoel S " is reputed to consist of 55–60% dipentene, 20–25% terpinolene, 15–20% of pinene terpinene and fenchene, 5–7% of cymene and *p*-menthane. Dipentene is somewhat similar to turpentine, but it oxidises at only one-seventh of the rate of the latter. It is a solvent for rubber, rubber chloride, some bakelites and glyptals, ester gum, cumarone, colophony, waxes, metallic driers and partly for kauri. It does not dissolve cellulose acetate or nitrate. It is compatible with most of the usual resin-oil combinations for which it is a good dispersing medium, and with which it reduces " skinning " and gelling, and also retards initial hardening.

Turpentine

Turpentine varies quite widely in composition, according to its source and method of manufacture. There are four types of turpentine recognised industrially, the best being gum spirit turpentine, consisting mainly of α-pinene, obtained by steam distilling the oleo-resin exudation from various coniferous trees, such as *Pinus palustris* and *P. heterophylla* in *America*, and *P. maritima* in France.

A second variety of turpentine known as wood turpentine is obtained by steam-distilling the chips or stumps remaining after the pines are cut down for lumber, and a third variety from the same material by destructive distillation ; these wood turpentines consist largely of dipentene. The fourth variety of industrial turpentine, known as sulphate turpentine, is obtained as a by-product in the manufacture of paper from wood ; sulphate turpentine contains carene as one of its chief constituents.

British Standard Turpentine,[2] *Type* 1, No. 244—1936 [2] consists of refined gum spirits of turpentine having the following characteristics : S.G. ·862–·872. B.R. below 150° C. 1% max. below 170° C. 95% min. Residue 3% max. R.I. 1·469–1·478. Residue unpolymerisable by sulphuric acid, 11% max. F.P. 90° F. min.

British Standard Turpentine,[2] *Type* 2, No. 290—1936[2] is distilled from oleo-resins or wood by steam or destructive distillation, and has S.G. ·859–·875. B.R. below 150° 1% max. ; below 170°, 70% min. ; below 180°, 90% min. Residue 2% max. R.I. 1·463–1·483. Residue unpolymerisable by sulphuric acid 16% max. F.P. 90° min.

The American Society for Testing Materials [3] recognises all four of the varieties described above, the specifications being as follows :—

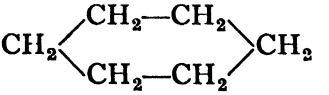
A.S.T.M. Spirits of Turpentine, D13–34 [3]

	Gum Spirits of Turpentine.		Wood Turpentine.					
			Steam Distilled.		Sulphate.		Destructively Distilled.	
	Maximum.	Minimum.	Maximum.	Minimum.	Maximum	Minimum.	Maximum.	Minimum.
Specific gravity 15 5/15·5 C.	0 875	0 860	0 875	0 860	0 875	0 860	0 866	0·860
Refractive index at 20 C., D line	1·478	1·465	1·478	1·465	1·478	1 465	1·483	1·463
Residue after polymerisation with 38N H_2SO_4, Volume per cent	2	—	2	—	2	—	2	—
Refractive index at 20 C.	—	1·500	—	1 500	—	1·500	—	1·480
Initial boiling point at 760 mm. pressure, deg C	160	150	160	150	160	150	157	150
Distilling below 160 C. at 760 mm. pressure, per cent.	—	90	—	90	—	90	—	60
Distilling below 180 C. at 760 mm pressure per cent	—	—	—	—	—	—	—	90

Turpentine also has L.H. 68. S.H. ·45. Dielec. const. 2·26. K.B.V. 50–90. Vis. 1·6. Auto-ignition temp. 253° C.

Rosin Spirit

Rosin spirit or rosin oil or pinolin, is obtained by the distillation of colophony; commercial products vary considerably in composition. Refined spirit has approximately the following characteristics: S.G. ·890–·930. B.R. 150°–300°, viz. 150°–200° 25%, 200°–250° 20%, 250°–270° 50%, 250°–300° 5%. R.I. 1·48–1·50. F.P. 266° F. (130° C.).

Cyclohexane. 

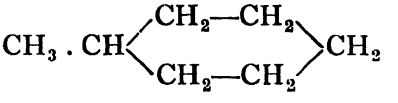
Cyclohexane, known also as hexamethylene, naphthene, and hexahydrobenzene, is a hydrocarbon somewhat similar to benzene and is now available technically.[6] It is manufactured by the catalytic hydrogenation of benzene; it occurs in Caucasian petroleum. It is a colourless, mobile liquid, having a less pungent odour than benzene and reminds of carbon tetrachloride. It is probably less toxic than benzene, and can replace benzene where the toxicity of this is objectionable. Cyclohexane is a good solvent for rubber, bitumen, caoutchouc, paraffin wax, but does not dissolve cellulose esters.

Physical Characteristics: Pure. S.G. at 20° C. 7784. R.I. 1·426. B.P. 81° C. S.P. 6·5° C. V.P. 77. F.P. −17° C. (1° F.). Vis. ·96. Dielec. const. 2. L.H. 86. S.H. ·497. Cub. exp. ·0011.

It forms the following constant boiling mixtures :—

Cyclohexane 45%.	Benzene 55%.	B.P. 77·8° C.
,, 63%.	Methyl alcohol 37%.	,, 54·2° C.
,, 70%.	Ethyl alcohol 30%.	,, 64·9° C.
,, 67%.	Isopropyl alcohol 33%.	,, 68·6° C.
,, 80%.	*n*-Propyl alcohol 20%.	,, 74·3° Co.
,, 86%.	Isobutyl alcohol 14%.	,, 78·1° C.
,, 90%.	*n*-Butyl alcohol 10%.	,, 79·8° C.

Methyl Cyclohexane



Known also as hexahydrotoluene, is produced by the hydrogenation of toluene and by the interaction of benzene and methane at high temperatures. It occurs naturally in Russian and Galician petroleum and in cracked petroleums.

Physical Characteristics: Pure. S.G. at 20° C. ·760. R.I. 1·425. B.P. 101·2. M.P. −126° C. L.H. 77. S.H. ·443. Dielec. const. 2·1. Vis. ·64. F.P. 25° D. (−4° C.).

Hydrogenated Solvent Naphtha

Hydrocarbons, having good solvent power for synthetic resins of the Rezyl type, have been prepared by hydrogenating petroleum solvent naphthas. These products are miscible with blown castor oil, and more closely resemble the coal-tar solvent naphthas than do the original petroleum naphthas. The following table indicates the types of product obtainable [7] :—

No.	B.R °C.	Aniline point	F.P. (Tag.)°F.	Dimethyl Sulphate Value.	Kauri Butanol Value.
1	93–135	11° C.	below 60	24%	55·2
2	135–185	−18° C.	61	62%	75·6
3	185–215	−23° C.	135	87%	77·3
4	215–238	36° C.	190	100%	85·7

Petroleum Hydrocarbons

Many grades of petroleum hydrocarbon solvents are available, those which are quoted here are the types of petroleum solvents in general use ; they are selected fractions obtained by distillation and may vary widely in actual chemical composition.[15]

Petroleum Ethers. (Ligroins).

These are the most volatile fractions and are generally of narrow boiling range and high degree of purity.

	1	2	3
S.G.	·645	·669	·676
B.R.	40°60° C.	60°–70° C.	60°–80° C.
Aromatics . . .	1%	4%	5%

Certain grades are used for pharmaceutical purposes, the following are standardised :—

British Pharmacopœia quality : S.G. ·62–·70. B.R. 95% between 60°–70° C.

U.S Pharmacopœia quality : S.G. ·634–·660. B.R. 35°–80° C.

Industrial Special Boiling-point Spirits.

These include extraction benzines or naphthas, rubber solvents, lacquer diluents.

Extraction benzines vary widely in boiling range, specific gravity and aromatic hydrocarbon content ; almost any boiling range between the limits of 30° and 160° C. being available with specific gravities varying between ·70 and ·80, and aromatic contents between 6% and 45%. They are good solvents for all types of oils with the exception of castor oil, in general those benzines with high aromatic content are the better solvents. K.B.V. about 30. Dil. rat. for cellulose acetate in acetone about 1·1 and for cellulose nitrate in butyl acetate about 1·2.

Rubber Solvents. Several types of petroleum solvents are used in processing rubber. For the preparation of solutions of rubber used for dipping and for the manufacture of moulded articles solvents having a boiling range of 115° to 160° C. are preferred. More volatile spirits having a boiling range of 70°–120° C. are used for work where rapid drying is required, while for cold vulcanisation processes a still lower boiling

range is preferred such as 30°–100° C. In general a high aromatic content leads to rubber solutions of low viscosity, prolonged milling of the rubber also reduces the viscosity of the solutions.

The following figures indicate the solvent characteristics of this class, K.B.V. about 37. Dil. rat. for cellulose nitrate in butyl acetate about 1·2 ; in acetone about 1·1 ; for cellulose acetate in acetone about 1·2.

Lacquer Diluents. Hydrocarbons are non-solvents for cellulose esters but they are used to reduce the cost of, to adjust viscosities and to permit the incorporation of certain resins into cellulose lacquers ; for these purposes the aromatic hydrocarbons are superior as their precipitating effects on the cellulose esters are not so pronounced. Nevertheless, paraffin hydrocarbon distillates of high aromatic content can often be used successfully and certain grades may replace benzene, toluene and xylene if due allowance is made for the different dilution ratios ; the following are typical distillates :

Benzene substitute . .	S.G. ·772	B.R. 75°– 95° C.	Aromatics 27%
Toluene substitute . .	,, ·795	,, 100°–120°	,, 45%
Xylene substitute . .	,, ·800	,, 115°–160°	,, 45%

The dilution ratios for cellulose nitrate in butyl acetate are of the order 1·5 to 2·0 as compared with about 2·7 for the aromatic hydrocarbons. The dilution ratios for paraffin distillates of low aromatic (*e.g.* below 20%) content vary between 1 and 1·25.

Paint and Varnish Solvents.

These include qualities known industrially as white spirit ; petroleum or mineral spirits ; paint and varnish thinner ; varnish makers' and painters' naphtha ; petroleum solvent naphtha.

White spirit has been standardised both in Britain and the U.S.A. and is generally regarded as a turpentine substitute ; it is sometimes termed mineral turpentine.

British Standard White Spirit No. 245—1936. B.R. up to 150° 10% max. ; below 190° 80% min. Residue ·2% max. at 100° C., ·5% max. at 60° F. F.P. 78° F. min. Neutral Free from objectionable sulphur compounds.

Stoddard Solvent A.S.T.M. D484—40. F.P. 100° F. min. B.R. up to 176° C. 50% min., up to 190°. 90% min. Final B.P. 210° C. max.

Petroleum or Mineral Spirits. A.S.TM. D235—39. F.P. 100° F. min. (38° C.). B.R. up to 350° F. (177° C.), 50% min. Final B.P. 210° C. max. Residue neutral.

Paint and Varnish Thinners. This is a general name for petroleum solvents used in the paint and varnish industry and covers a range of distillates with boiling ranges up to about 250° C. max.

V.M. and P. Naphtha. A distillate known in America as varnish makers' and painters' naphtha which is somewhat more volatile than white spirit. B.R. about 100°—160° C.

High Aromatic Petroleum Solvent Naphthas. These are distillates recently introduced for use with high temperature baking coatings; three qualities are produced having the following approximate characteristics:

	1	2	3
S.G.	·833	·860	·883
B.R.	100°–140° C.	130°–180° C.	175°–210° C.
F.P. (Tag.)	—	85° F.	126° F.
Aromatics	73%	93%	—
Kauri butanol value	91	93	84

Petroleum distillates are in general solvents for beeswax, carnauba wax, montan wax, Japan wax, paraffin wax,[16] ceresin, spermaceti, bitumen, rubber, ester gum, dammar and elemi, their solvent powers generally increasing with increase in aromatic and naphthenic hydrocarbon content and diminishing with rise in boiling point. They do not dissolve cellulose esters or ethers, shellac, pontianac, manila, copals, sandarac, chlorinated rubber, polystyrene.

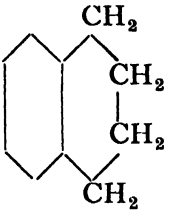
The characteristics of a few pure saturated aliphatic hydrocarbons are quoted below as a guide.

	B.P.	S.G. 20° C.	S.P.	V.P	L.H.	S.H.	R.I.
n-Pentane	36·0° C.	·626	—130	422	84	·540	1·368
n-Hexane	68·7° C.	·659	—95	120	82	·531	1·375
n-Heptane	98·4° C.	·684	—91	36	76	·531	1·388
n-Octane	125·6° C.	·703	—57	10	71	·518	1·398
n-Nonane	150·7° C.	·718	—54	3·2	—	·523	1·406
n-Decane	173·8° C.	·730	—30	2·7	60	·520	1·412

Hydroterpin.

This substance is a product of the hydrogenation of turpentine,[7] and has a similar mild odour. B.R. 180–195°. S.G. ·879 at 20°. R.I. 1·4733.

Tetrahydronaphthalene.



1 . 2 . 3 . 4 Tetrahydronaphthalene, known commercially under the trade-mark name "Tetralin," [9] is a product obtained by the partial catalytic hydrogenation of naphthalene, one ring being completely hydrogenated, the other remaining unchanged. This is effected by conducting the hydrogenation in the vapour phase.

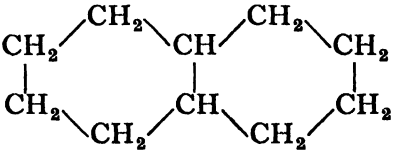
It is a non-toxic liquid which oxidises on exposure to air, like turpentine, forming substances which decompose violently on sudden heating.[12]

Physical Characteristics: S.G. ·973–·980. B.R. 205°–215°. R.I. 1·540–1·547. F.P. 78° C. (172° F.). L.H. 79. S.H. ·40. Vis. 2·2.

Tetrahydronaphthalene oxidises on heating in the presence of air and the boiling range widens.

It is a powerful solvent for oils, resins, waxes, rubber, cumarone, colophony, mastic, asphalt, most resinates, Albertols, and linoxyn. It does not dissolve cellulose esters, hard copals, shellac, bakelites, and is not miscible with alcohol (unless anhydrous) or water.

Decahydronaphthalene.



Decahydronaphthalene, known commercially under the trade-mark names "Dec" and "Decalin," [10] is produced by the complete hydrogenation of naphthalene or tetrahydronaphthalene, both in the liquid state, at temperatures ranging from 150° C. upwards, 190° C. being the most favourable. It is a non-toxic liquid, having the following physical characteristics: S.G. ·887–·890. B.R. 183°–192°. R.I. 1·467–1·479.

F.P. 57° (135° F.). Auto-ignition temp. 262° C. M.P. −124°. S.H. ·3874. L.H. 71. E.R. 2·6 (Turpentine = 1). Dielec. const. 2·1. Vis. 1·9.

It is not such a powerful solvent as tetrahydronaphthalene and does not undergo atmospheric oxidation. Solvent for fats, waxes, rubber, dammar, mastic, manila. Non-solvent for cellulose esters, copal, kauri, linoxyn. Non-miscible with water or alcohol (unless anhydrous), but miscible with most organic solvents.

Carbon Di-sulphide. CS_2

Carbon di-sulphide is a colourless, highly volatile liquid which becomes yellow with age and under the influence of light. It has an ethereal odour which is more or less pleasant, according to the impurities present.

It is a solvent for sulphur, rubber, vegetable oils and ester gum ; it gels ethyl and benzyl cellulose, but does not dissolve cellulose acetate or nitrate or vinyl resins.

British Standard Specification[2] *No.* 662—1936. S.G. 1·270–1·274 (1·265–1·269 at 20°). B.R. up to 46·4°. 95% min. Residue ·01% max. Neutral to methyl red ; free from H_2S.

The pure substance has B.P. 46·25°. M.P. −111·6°. F.P. −22° C. Auto-ignition temperature 125° C. L.H. 84 ; S.H. ·24. R.I. 1·635. Water dissolves ·2%. Dielec. const. 2·67. Elec. cond. $3·7 \times 10^{-3}$. Vis. ·365.

Carbon di-sulphide is dangerously inflammable, mere contact with a hot steam pipe or an electric lamp bulb is sufficient to cause the vapour to ignite by reason of its extremely low auto-ignition temperature. The explosive limits of mixtures with air lie between 1% and 50% by volume.

Carbon di-sulphide is narcotic in high concentration and is a severe chronic nerve poison.

The following ageotropic mixtures are known :—

Carbon di-sulphide	14%.	Methyl alcohol 86%.	B.P. 37·7°
,, ,,	8%.	Ethyl alcohol 92%.	,, 42·4°
,, ,,	7%.	Isopropyl alcohol 93%.	,, 44·6°
,, ,,	32·5%.	Acetone 67·5%.	,, 39·2°
,, ,,	15%.	Methyl ethyl ketone 85%.	,, 45·9°
,, ,,	36·5%.	Ethyl formate 63·5%	,, 39·4°
,, ,,	30%.	Methyl acetate 70%.	,, 40·2°
,, ,,	99%.	Ethyl ether 1%.	,, 34·5°

Nitroparaffins

The nitroparaffins [12] are new solvents of considerable interest, they are produced by reacting aliphatic hydrocarbon gases with nitric acid under pressure at high temperatures.

The following table gives the physical properties of the more important nitroparaffins :—

	Nitro-methane.	Nitro-ethane.	1-Nitro-propane.	2-Nitro-propane.
S.G. at 20° C.	1·139	1·052	1·003	0·992
R.I.	1·3818	1·3916	1·4015	1·3941
B.P. °C.	101·2	114·0	131·6	120·3
M.P. °C.	−29	−90	−108	−93
F.P. °F.	112	106	120	103
V.P.	27·8	15·6	7·5	12·9
E.R. (Butyl acetate = 1)	180	145	100	124
S.T.	37	31	30	30
*p*H at 25° C.	6·4	6·0	6·0	6·2
Water dissolves %	9·5	4·5	1·4	1·7
Dissolves water %	2·2	0·9	·05	0·6

The nitropropanes are solvents for cellulose nitrate, ethyl cellulose, benzyl cellulose, ester gum, cumarone, glyptals, rubber chloride, polyvinyl aceto-chloride, cellulose aceto-propionate, cellulose aceto-butyrate, vegetable oils, castor oil and petroleum hydrocarbons. In the presence of alcohol they are good solvents for cellulose acetate, kauri, manila, pontianack. They do not dissolve rosin, tars, pitches, waxes, casein, gelatine, zein, congo or shellac.

They are colourless, non-hygroscopic liquids of mild odour but there are indications that they are toxic,[13] about 0·1% in air may be assumed to be dangerous, causing irritation of the central nervous system. The toxicity of the nitroparaffins increases with molecular size.[14]

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CHAPTER II

ALCOHOLS AND THEIR ETHERS

Methyl Alcohol. $CH_3 . OH$

METHYL alcohol or methanol, as it is now more frequently termed, is an important solvent, the manufacture of which has attracted very considerable attention during the last decade.

Until recent times it was manufactured entirely by the distillation of wood along with acetic acid, acetone (*q.v.*) and other substances (*cf.* Wood spirit). Methanol made by modern synthetical methods from water-gas has now almost displaced the " natural " product, although it is unlikely that complete replacement will ever occur.

The most important synthetical method is that originally discovered by Sabatier in 1905,[1] who effected the catalytic combination of carbon monoxide and hydrogen.[2] In 1913 the Badische Anilin-und Soda Fabrik patented [3] the use of a wide range of catalysts for promoting the conversion of the constituents of water-gas into a complex mixture of methyl and other alcohols, aldehydes and ketones. A variety of patents quickly followed, but perhaps the most outstanding work is that of Patart in France, who used as raw materials either carbon monoxide and hydrogen [4] or methane and oxygen.[5] Thus one volume of carbon monoxide with one and a half to two volumes of hydrogen at 150 to 200 atmospheres pressure, passed over zinc oxide at a temperature of 400° to 420° C., gives a liquid product which consists mainly of methyl alcohol and water with traces of aldehydes and acetone. Similarly, water-gas and hydrogen at 500 atmospheres pressure give methyl alcohol in a yield of 80%, together with traces of higher alcohols, acids, water and ammonia but no acetone, 300 cubic metres of water-gas yielding 100 litres of methyl alcohol. Patart also found that methane mixed with one-half its volume of oxygen, when passed over coke at a temperature of 800° to 1,000° C., yields a gas consisting of two volumes of hydrogen with one volume of carbon monoxide, this mixture, on further catalytic treatment as above, yielding a liquid consisting mainly of methyl alcohol.[6] Further, coal gas or coke-oven gas, passed over

zinc oxide or chromium sesquioxide at a temperature of 300° and under a pressure of 150 to 200 atmospheres, similarly yields a liquid consisting of methyl alcohol and hydrocarbons [7]; the hydrocarbons, on further catalytic treatment, give higher alcohols in considerable yield. The addition of alkali hydroxides or carbonates to the usual catalysts causes an increase in the proportion of higher alcohols.[8] It is not unlikely that this process may be developed to one of considerable industrial importance for the manufacture of higher alcohols in the near future, although the technical difficulties are considerable.

It has also been proposed to manufacture methyl alcohol from methane by chlorination [9] and treatment of the resulting methyl chloride with alkali acetates.[10] This process is closely linked with that for the production of methylene dichloride and chloroform (*q.v.*).

Methyl alcohol is known in America as Columbus spirit, although methanol is the term now usually applied there.

Characteristics : Pure. S.G. ·796. B.P. 64·7°. V.P. at 20° 95 mm. F.P. 32° F. I.P. 32° F. M.P. −97°. R.I. 1·329. S.H. ·597. L.H. 263 Elec. cond. 3×10^{-7}. Dielec. const. 31. Cub. exp. ·00118. Vis. ·61.

British Standard Methyl Alcohol.[11] S.G. ·799 max. B.R. 64·5–65·5 (95%); acidity ·004% max. as acetic acid. Residue ·01% max.; aldehydes and ketones ·06% max. as acetone; sulphur (total) ·001% max.; completely miscible with water in all proportions.

Anhydrous methyl alcohol is clearly miscible with benzene in all proportions. It does not form a constant-boiling mixture with water, but it does so with many organic solvents. The following are known :—

Methyl alcohol 15%.	Acetone 85%.	B.P. 55·9°
,, 19%.	Methyl acetate 81%.	,, 54·0°
,, 40%.	Benzene 60%.	,, 58·3°
,, 62%.	*n*-Heptane 38%.	,, 60·5°
,, 27%.	*n*-Hexane 73%.	,, 50·0°
,, 21%.	Carbon tetrachloride 79%.	,, 55·7°
,, 49%.	Trichlorethylene 51%.	,, 60·2°
,, 37%.	Cyclohexane 63%.	, 54·2°
,, 16%.	Ethyl formate 84%.	,, 51·0°
,, 47%.	Ethyl acetate 53%.	,, 74·0°
,, 14%.	Carbon disulphide 86%	,, 37·6°
,, 12%.	Chloroform 88%.	,, 54·0°

Pure methyl alcohol dissolves neither cellulose acetate nor high-viscocity nitrate, but the presence of a relatively small proportion of acetone renders it a potent solvent for the nitrate and, to a less degree, for the acetate. It dissolves " ½ sec." cellulose nitrate fairly readily. It is a solvent for ethyl cellulose, colophony, benzyl abietate, soft bakelites, castor oil, and is miscible with aromatic hydrocarbons. It partially dissolves shellac, mastic, and soft copals. It is non-miscible with linseed oil and with petroleum hydrocarbons.

Ethyl Alcohol. $C_2H_5 . OH$

Ethyl alcohol or ethanol has been very largely used in conjunction with ethyl ether as a solvent for cellulose nitrate in the manufacture of celluloid. This mixture is now seldom used for lacquer work. Alcohol, by itself, is not generally a solvent for cellulose nitrate or acetate, although anhydrous alcohol will dissolve some of the lower nitrated forms of cellulose. The solvent properties of alcohol rapidly decrease with increasing proportions of water; alcohol containing 5% of water is practically a non-solvent for all forms of cellulose nitrate.

Anhydrous alcohol dissolves colophony, sandarac, kauri, pontianac, manila, elemi, mastic, thus, dammar, shellac, gum camphor and heat-treated congo and zanzibar; an addition of 20 to 30% of benzene renders it a solvent for benzyl cellulose, ester gum, and cumarone. It dissolves ethyl cellulose readily and solutions up to 16% by vol. can be made; such solutions may be clarified by the addition of a small proportion of toluene if necessary. It is a solvent for certain synthetic resins such as the soft bakelites, abralac, acetaldehyde resin, acrolein resin, furfural resin, cyclohexanone resin, and cyclohexanone-formaldehyde resin. It is miscible with castor oil and hydrocarbons.

Pure anhydrous alcohol has the following characteristics: S.G. ·7937. B.P. 78·3°. V.P. at 20° 44 mm. L.H. 209. S.H. ·588. M.P. −120°. R.I. 1·3619. F.P. 57° F. (14° C.); I.P. 59° F. Vis. 1·2. Elec. cond. $1·4 \times 10^{-9}$. Dielec. const. 26. Cub. exp. ·00108.

British Standard Alcohol No. 507—1933 [11] (not denatured) has: S.G. ·8171 equivalent to 66° overproof (92% by weight, 94·7% by volume). Acidity, ·005% max. of sulphuric acid. Aldehyde ·1% max. as acetaldehyde. Residue ·01% max. Shows no turbidity with 5 volumes of distilled water.

Methylated spirit varies in composition. A form most suitable for lacquer manufacture consists essentially of the British Standard alcohol quoted above denatured with 5% of methyl alcohol and is more usually termed *industrial alcohol.*

The following azeotropic mixtures are known :—

Ethyl alcohol	95·57%.	Water 4·43%.	B.P. 78·15°
,,	32·37%.	Benzene 67·63%.	,, 68·24°
,,	68·0%.	Toluene 32·0%	,, 76·7°
,,	21·0%.	*n*-Hexane 79·0%	,, 58·6°
,,	48%.	*n*-Heptane 52%.	,, 72·0°
,,	30·5%.	Cyclohexane 69·5%.	,, 64·9°
,,	30·6%.	Ethyl acetate 69·4%.	,, 71·8°
,,	15·85%.	Carbon tetrachloride 84·15%	,, 64·95°
,,	7·0%.	Chloroform 93·0%.	,, 59·4°
,,	27·0%.	Trichlorethylene 73·0%.	,, 70·9°
,,	81·0%.	Tetrachlorethylene 19·0%.	,, 77·95°
,,	81%	Perchlorethylene 19%.	,, 78·0°
,,	9·0%.	Carbon disulphide 91·0%.	,, 42·4°
,,	40·0%.	Methyl ethyl ketone 60·0%.	,, 74·8°

and a ternary mixture containing ethyl alchol 38%, water 12%, toluene 50%. B.P. 74·6° C.[32]

n-Propyl Alcohol. $CH_3 . CH_2 . CH_2 . OH$

Propyl alcohol or propanol is one of the chief constituents of fusel oil, from which it is isolated in a state of high purity. In its properties it is similar to isopropyl alcohol, to which it is superior as a lacquer diluent on account of its higher boiling-point, being therefore less likely to cause chilling. It is miscible with all the usual solvents and with water in all proportions. The pure alcohol boils at 97·15°, has S.G. ·805, M.P. −127°, F. P. 22° C., R.I. 1·386. S.H. ·586 at 25°. L.H. 163 cal./gm. Vis. 2·3. Elec. cond. 9×10^{-9}. Dielec. const. 22. The usual boiling range for the technical article is 95°–102°. It forms a number of constant-boiling mixtures, of which the following are of interest :—

n-Propyl alcohol	71·7%.	Water 28·3%.	B.P. 87·7°
,,	20%.	Cyclohexane 80%.	,, 74·3°
,,	4%	*n*-Hexane 96%.	,, 65·6°
,,	17%.	Benzene 83%.	,, 77·1°
,,	49%.	Toluene 51%.	,, 92·6°
,,	74%.	*n*-Octane 26%.	,, 95·0°
,,	11·5%.	Carbon tetrachloride 88·5%.	,, 72·8°
,,	54%.	Tetrachlorethylene 46%.	,, 94·0°
,,	54%.	Perchlorethylene 46%.	,, 94·0°

n-Propyl alcohol 80%.	Monochlorbenzene 20%.	B.P. 96·5°
,, 57%.	Diethyl ketone 43%.	,, 94·9°
,, 40%.	*n*-Propyl acetate 60%.	,, 94·2°
,, 9·8%.	*n*-Propyl formate 90·2%.	,, 80·6°
,, 51%.	Ethyl propionate 49%.	,, 93·4°

It is a solvent for colophony, soft copals, shellac, soft bakelites, ester gum, benzyl abietate, urea-formaldehyde resins, castor, linseed and other oils. It does not dissolve cellulose esters, but has a solvent action on some cellulose ethers.

Isopropyl Alcohol. $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH\,.\,OH$

Isopropyl alcohol, known also as isopropanol and secondary propyl alcohol, has been largely used as a substitute for ethyl alcohol, mainly in perfumery and medicine. It is not a usual constituent of normal fusel oils, but is manufactured either from acetone or from the olefine gases arising from the cracking of petroleums.

There are several processes in operation for the preparation of isopropyl alcohol from acetone, all depending on the catalytic addition of hydrogen by passing acetone and hydrogen gas over heated nickel catalyst. The processes vary mainly in the degree of pressure, time of contact, temperature, and means of supporting the nickel catalyst.[12] Thus acetone in the vapour state is readily hydrogenated at 115° to 125° C., whilst under pressures sufficiently high to keep the acetone liquid temperatures between 250° and 300° are used. The catalyst can be either of the " rigid " or the " non-rigid " type, the former being in the form of nickel turnings which have been activated first by anodic oxidation in sodium carbonate solution, followed by reduction in hydrogen at temperatures ranging from about 180°–300° C. The non-rigid type of catalyst consists of kieselguhr or some similar " support " upon which hydrated nickel carbonate has been precipitated, followed by roasting and reduction in hydrogen at 250° C.[13]

Granular nickel catalyst has also been used, the acetone being distilled over it in an atmosphere of hydrogen at 100 atmospheres pressure.

The manufacture of isopropyl alcohol from petroleum is conducted briefly as follows. Petroleum fractions of high-boiling range are " cracked " by treatment at a high temperature, this cracking process giving rise to petroleums of low-

boiling range and to a large quantity of gas. The gas has an olefine content of about 10 to 15%, and contains ethylene, propylene, butylenes, and amylenes; it is first freed from sulphur compounds, and then passed up through a series of absorption towers, down which are sprayed sulphuric acid solutions of graduated strengths, so as first to absorb the amylenes and butylenes, then the propylene and finally the ethylene.[14] The acid and gas are also circulated counter-current-wise so that the fresh gas meets the diluted acid, and *vice versâ*. After absorption of the olefines the saturated acid is mixed with water, thus causing higher alcohols and polymerised olefines to separate out as an oil layer; the clear acid solution is then steam-distilled and crude isopropyl alcohol obtained (*cf.* secondary butyl alcohol and synthetic amyl alcohol). The crude alcohol is subjected to fractional distillation and is obtained in a high state of purity.

The pure alcohol has an odour slightly stronger than that of ethyl alcohol, and its taste is slightly bitter. It is a stable colourless liquid, miscible with water in all proportions. B.P. 82·4°. S.G. ·790, V.P. 32, M.P. −89°, F.P. 12° C. (53° F). R.I. 1·3776. L.H. 162. H.C. 7970. S.H. ·61 at 20° C. Vis. 2·4. Cub. exp. ·00107. Elec. cond. 5×10^{-7}. Dielec. const. 14.

D.T.D. 389—1942 [33] requires: S.G. ·788–·793. B.R. 80—83° (98% min.) Residue 02·% max. No turbidity of water. R.I. 1·3773–1·3800. *p*H 5·8–7·0.

It forms the following constant-boiling mixtures:—

Isopropyl alcohol	87·7%.	Water 12·3%.	B.P. 80·4°
,,	33%.	Cyclohexane 67%.	,, 68·6°
,,	33%.	Benzene 67%.	,, 71·9°
,,	22%.	*n*-Hexane 78%.	,, 61·0°
,,	69%.	Toluene 31%.	,, 80·6°
,,	8%.	Carbon disulphide 92%.	,, 44·6°
,,	30%.	Methyl ethyl ketone 70%.	,, 77·3°
,,	23%.	Ethyl acetate 77%.	,, 74·8°
,,	52%.	Isopropyl acetate 48%.	,, 80·1°
,,	14%.	Carbon tetrachloride 86%.	,, 67·0°
,,	45%.	Ethylene dichloride 55%.	,, 74°
,,	28%.	Trichlorethylene 72%.	,, 74°
,,	81%.	Tetrachlorethylene 19%.	,, 81·7°

And with 7·5% of water and 73·8% of benzene boiling at 66·5°.

Isopropyl alcohol is not a solvent for cellulose esters, but

has distinct latent solvent properties, the presence of a relatively small quantity of an ester rendering it a solvent for cellulose nitrate. It dissolves cyclohexanone-formaldehyde resin, colophony, mastic, kauri, sandarac ; it partly dissolves shellac, elemi, dammar and copal.

It has the advantage over industrial alcohol in that it is anhydrous and therefore less likely to cause water blush. The fact that no methylation is required is also in its favour, since methylating agents not infrequently affect the strength of cellulose films.

n-Butyl Alcohol. $CH_3 . CH_2 . CH_2 . CH_2 . OH$.

n-Butyl alcohol, known also as butanol, is of extreme industrial importance, since it serves as a raw material for the manufacture of *n*-butyl acetate, the most widely used of the cellulose-nitrate solvents.

n-Butyl alcohol is mainly manufactured by two processes ; a large part of the butyl alcohol of commerce is produced by the fermentation process developed by Strange, Graham, Fernbach, Weizmann and others ; an improved process is now in operation.[15] The Weizmann process consists in preparing a wash from maize flour by heating with water to 130°–140° C. under two to three atmospheres pressure for three to four hours ; inoculating the cooled, sterile wash with a specially prepared culture, fermenting for about forty-eight hours, and distilling the fermented wash, thus obtaining about 20 lb. of crude solvent for every hundredweight of maize flour. This crude solvent consists mainly of acetone, and *n*-butyl alcohol with small quantities of ethyl alcohol, primary amyl alcohol, *n*-hexyl alcohol and their esters of acetic, *n*-butyric, caprylic and caproic acids. The *n*-butyl alcohol is separated from the wash by means of a continuous Coffey still, from which it is obtained with a dissolved water-content of about 9%. The anhydrous alcohol results on fractional distillation, the water coming over in the first fractions as a binary mixture, containing 37% of water.

Butyl alcohol is also manufactured in very large quantities from acetaldehyde, itself obtained either from acetylene by hydration in the presence of a mercury salt or from alcohol by limited oxidation or dehydrogenation. Acetaldehyde is converted *viâ* aldol to crotonaldehyde, which is hydrogenated to *n*-butyl alcohol.

Butyl alcohols have also been made from water gas and

hydrogen [16] or from coal gas and coke-oven gas by catalytic treatment under pressure, and at high temperatures (*vide* methyl alcohol).[17] Ethyl alcohol circulated over magnesium, calcium, barium or manganese oxide at 400°–500° C. forms butyl alcohol, esters and acetals, in 20 to 30% yield. The use of a catalyst consisting of 60 to 80% of magnesium oxide and 20 to 40% of copper oxide at a temperature between 270° and 325° and under 200 to 300 atmospheres pressure has also been proposed.[18]

Contrary to statements sometimes made, *n*-butyl alcohol is not a normal constituent of fusel oils.

Pure butyl alcohol has S.G. ·8097 at 20°, ·813 at 15°; R.I. 1·397. B.P. 117·7°. M.P. -90°. F.P. 35° C. (95° F.). Vis. 3. Cub. exp. ·00095. V.P. 5 mm. at 20° C., S.H. ·565 at 20°. L.H. 141. Elec. cond. 9×10^{-9}. Dielec. const. 18.

British Standard Specification No. 508—1923[11]. *Butyl alcohol* has S.G. ·810–·816. B.R. 115°–118° (95%). Acidity ·01% max. as acetic acid, aldehydes ·5% max. as butyraldehyde. Residue ·01% max. F.P. 80° F. (27° C.) min.

A.S.T.M. Specification. Normal butyl alcohol D304–40 [19] has: S.G. ·810–·815 at 20°. B.R. up to 100°, none; 105°, 2% max.; 115° 10% max.; above 118°, none. Residue, ·005% max., acidity ·03% max.

The mutual solubilities of water and butyl alcohol are as follows:—

Temperature	Solubility of butyl alcohol in water	Solubility of water in butyl alcohol.
0° C.	10·5% by weight	—
10° C.	8·9% ,,	19·7
20° C.	7·8% ,,	20·0
30° C.	7·1% ,,	20·6
40° C.	6·6% ,,	21·4
50° C.	6·5% ,,	22·4
60° C.	6·5% ,,	23·6
70° C.	6·7% ,,	25·2
80° C.	6·9% ,,	26·4
90° C.	7·9% ,,	30·1
100° C.	9·2% ,,	33·8
110° C.	10·5% ,,	37·6
120° C.	16·1% ,,	46·0

n-Butyl alcohol forms the following binary constant-boiling mixtures:—

n-Butyl alcohol 57·6%.	Water 42·4%.	B.P. 92·6° C.
,, 73%.	*n*-Butyl acetate 27%.	,, 116· C.
,, 23·7%.	*n*-Butyl formate 76·3%.	,, 105·8° C.
,, 33%.	Methyl iso-valerate 67%.	,, 113° C.
,, 10%.	Cyclohexane 90%.	,, 79·8° C.
,, 32%.	Toluene 68%.	,, 105·5° C.
,, 32%.	Perchlorethylene 68%.	,, 110·0° C
,, 20%	Ethyl isobutyrate 80%.	,, 108·5° C

Two ternary mixtures are of interest, viz.: Butyl alcohol 10% ; butyl formate 68·7% ; water 21·3% ; B.P. 83·6. Butyl alcohol 27·4% ; butyl acetate 35·3% ; water 37·3% ; B.P. 89·4.

Butyl alcohol possesses the unique property of being a solvent for hard copals ; it dissolves kauri, congo, manila, dammar, sandarac, elemi, shellac, ester gum, cyclohexanone-formaldehyde and urea-formaldehyde resins, benzyl abietate, calcium, zinc and magnanese resinates, castor and linseed oils. It partly dissolves mastic and cumarone ; it is miscible with hydrocarbons. It does not dissolve cellulose esters or ethers or rubber chloride. The addition of a small quantity (3%) will bring about homogeneous mixing of methylated spirit with petroleum hydrocarbons. Ethyl cellulose dissolves in mixtures of butyl alcohol and xylene.

Iso-butyl Alcohol. $\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>\!CH—CH_2 \,.\, OH$

Known also as iso-propyl carbinol and as 2-methyl propanol 1, is a primary alcohol occurring in fusel oil from which it is isolated by distillation. Although obtainable industrially, its use is limited, as it has no marked advantage over normal butyl alcohol, which it resembles in solvent properties.

Characteristics : S.G. ·8057. B.P. 108°. R.I. 1·397. M.P. –108°. F.P. 22° C. (72° F.). V.P. 8·8. S.H. ·665. L.H. 138. Vis. 3·9. Elec. cond. 8×10^{-8}. Dielec. const. 18. Cub. exp. ·00095. Water dissolves 10% at 15°. Dissolves 15% of water at 15°.

The following constant-boiling mixtures are known :—

Iso-butyl alcohol 67%.	Water 33%.	B.P. 90·0° C.
,, 14%.	Cyclohexane 86%.	,, 78·1° C.
,, 9%.	Benzene 91%.	,, 79·8° C.
,, 44%.	Toluene 56%.	,, 101·1° C.

Secondary Butyl Alcohol. $\begin{matrix}CH_3\\ \\ C_2H_5\end{matrix}\!\!>\!CH\,.\,OH$

Known also as methyl ethyl carbinol and as butanol 2. It is made by hydrogenating methylethyl ketone, and also from the butylenes arising from the cracking of petroleum hydrocarbons by processes similar to those used for the manufacture of isopropyl alcohol (*q.v.*). It is not widely used, but is available technically.

Characteristics : S.G. ·810–·815 B.R. 98°–102°. R.I. 1·397. F.P. 75° F. (24° C.). Solubility in water, 12·5%. B.P. (pure), 99·5°. S.G. at 20°, ·806. It is a solvent for ester gum, shellac, kauri, mastic, sandarac, elemi, castor and linseed oils, and aromatic hydrocarbons. It does not dissolve cellulose esters. Its odour is reminiscent of peppermint. It forms a constant-boiling mixture containing 27·3% of water boiling at 87·5°, and also one containing 13·7% sec. butyl acetate boiling at 99·6°.

Amyl Alcohol

There are eight isomeric amyl alcohols, and three of these eight exist each in two modifications, owing to the presence of asymmetric carbon atoms.

The amyl alcohol of commerce obtained from fusel oil is a mixture of two of the eight, viz., primary isoamyl alcohol and active amyl alcohol, known as isobutyl carbinol and sec. butyl carbinol also as 3-methylbutanol and 2-methylbutanol respectively, their formulæ being :—

$\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>\!CH\,.\,CH_2\,.\,CH_2\,.\,OH$ and $\begin{matrix}CH_3\,.\,CH_2\\ \\ CH_3\end{matrix}\!\!>\!CH\,.\,CH_2\,.\,OH$

the latter having an asymmetric carbon atom.

Synthetic amyl alcohol is also available, being produced in America and sold under the trade name "Pentasol." [20] Pentasol consists of a mixture of five of the eight isomeric amyl alcohols, and is manufactured from petroleum. The process begins with the isolation of a mixture of *n*-pentane and isopentane from light petroleum by fractional distillation, the fraction boiling between 28° and 39° C. being taken.

This pentane fraction is thoroughly dehydrated, vaporised and mixed in a tubular reaction vessel with chlorine gas. The mixture then passes through a gas-heated pipe still to con-

tinuous fractionating columns by means of which the unchlorinated pentanes and hydrochloric acid are separated from the amyl chlorides. The crude amyl chloride mixture is again fractionally distilled for the purpose of removing polychlorinated pentanes from the mono-chloro-pentanes The mono-chloro-pentane mixture thus obtained has the following approximate composition :—

1 Chloropentane	24%
2 ,, ...	8%
3 ,, ...	18%
2 Methyl 4 chlorobutane . . .	15%
2 ,, 2 ,, . . .	30%
2 ,, 2 ,, . . .	5%

The amyl alcohols are produced from this mixture by hydrolysis with sodium oleate solution in the presence of a catalyst. The process is made continuous by using two hydrolysing digestors in parallel, from one of which the products of the reaction pass to a series of fractionating columns while the hydrolysis is proceeding in the other digestor. The fractionating columns separate the amyl alcohols from the amylenes which are also produced and the unchanged amyl chlorides, these two latter being returned to the process. The amyl alcohol mixture finally obtained has the following approximate composition :—

Pentanol 1	26%
,, 2	8%
,, 3	8%
2 Methyl butanol 4	16%
2 ,, ,, 1	32%

There are also obtained tertiary amyl alcohol and diamyl ethers.

In another similar process [21] the mixture is treated with chlorine in an apparatus designed to regulate and limit the violence of the reaction, which, being exothermic, may proceed explosively. The apparatus consists of a lead-free glass tube of wide bore placed vertically ; near the bottom of the tube is a screen, upon which rests activated carbon to a depth of about 3 inches ; through the bottom of the tube, and through the screen, passes a small nozzle, by means of which the chlorine is injected into the funnel-shaped bottom end of a narrow glass tube placed concentrically within the larger one, and extending

about one half of the way up. The pentane is placed in the apparatus, so as to fill it to the extent of about three-quarters, and is exposed to ultra-violet light, which aids the reaction. The passage of the chlorine through the jet at the bottom causes both the pentane and the catalyst to circulate in intimate contact, and the reaction proceeds smoothly; any vapour which is given off is returned to the apparatus by means of a refrigerating condenser, the hydrochloric acid gas produced in the reaction passing away through this condenser. In order to prevent or limit the formation of poly-chloro derivatives, the chlorination is discontinued when 20 to 25% of the pentane has been chlorinated; the product is then neutralised and the five amyl chlorides, produced in the reaction, fractionally distilled out.

The purified amyl chloride mixture consists approximately of :—

1 Chloropentane	26%
2 ,, ...	18%
3 ,, ...	8%
2 Methyl 4 chlorobutane . . .	16%
2 ,, 2 ,, . . .	32%

The next stage in the process is the conversion of these chlorides to the corresponding acetates, and is conducted in autoclaves under a pressure of 200 to 205 lb. per square inch, and at a temperature of 200°–230° C., the reagent being a mixture of powdered sodium acetate and carbon. The heating is maintained for eight hours, and the course of the reaction can be followed by noting the gradual drop in pressure as the highly volatile amyl chlorides are converted into the acetates. When the reaction is complete the crude amyl acetate is distilled out, neutralised and redistilled. The mixture of amyl acetates thus obtained has approximately the following composition :—

Pentanol 1	B.P. 138° C. . .	4%
2 Methyl butanol 1	,, 128° C. . .	4%
3 ,, ,, 1	,, 131° C. . .	2%
Pentanyl acetate 1	,, 148° C. . .	21%
,, ,, 2	,, 134° C. . .	19%
,, ,, 3	,, 132° C. . .	8%
2 Methyl butanyl acetate 1	,, 142° C. . .	28%
3 ,, ,, ,, 1	,, 142° C. . .	14%

The ester-content of the mixture is over 85%. The alcohols are obtained by hydrolysis. Pentasol conforms with the following specification: S.G. at 20°, ·812–·820. B.R. 112°–340°. *Peramyl alcohol* has: S.G. ·883. B.R. 90°–160°, and is a mixture of cyclo-hexanol, iso-propyl alcohol and *n*-butyl alcohol.

Several of the isomeric amyl alcohols are now obtainable industrially [22] in a pure state, having the following characteristics :—

Pentanol 1	S.G. at 20°, ·82	B.R. 134·5–138·5 (95%)
Pentanol 2	,, ·81	,, 117·5–121·5
Pentanol 3	,, ·82	,, 113·6–117·6
3 Methyl butanol 1	,, ·815	,, 128·5–132·5
2 Methyl butanol 1	,, ·816	,, 125–131
1·1·Dimethyl propanol 1	,, ·810	,, 99·8–103·8

The following tables give the physical properties of six of the eight possible amyl alcohols.[23]

Amyl alcohol	S.G. 20°.	B.P. °C	F.P. °F.	L.H.	Binary mixture.	
					B.P.	% water
Pentanol 1	·817	138	134	102	95·5°	47·8
,, 2	·810	119	121	98	92·3°	32·2
,, 3	·815	115·7	124	97	91·4°	32·2
2 Methyl butanol 1	·816	128	135	100	93·8°	41·5
2 ,, ,, 2	·812	101·8	74	93	87·2°	22·0
2 ,, ,, 4	·812	130·5	132	100	95·0°	42·4

Solubility of Water in the Amyl Alcohols.

	Millilitres of alcohol dissolved in 100 ml. water.			
	10°.	30°.	50°.	70°.
Pentanol 1	6·4	7·2	8·5	10·7
,, 2	8·0	8·8	9·9	11·4
,, 3	8·2	9·1	10·2	11·8
2 Methyl butanol 1	7·0	7·8	9·2	11·3
2 ,, ,, 2	17·6	17·7	17·8	17·9
2 ,, ,, 4	6·5	7·4	8·7	10·8

Solubility of the Amyl Alcohols in Water.

	Millilitres of water dissolved in 100 ml. alcohol			
	10°.	30°.	50°.	70°.
Pentanol 1	2·6	2·1	1·9	1·8
,, 2	7·5	5·3	4·4	4·1
,, 3	8·0	5·5	4·5	4·2
2 Methyl butanol 1 . .	5·0	3·6	3·1	3·0
2 ,, ,, 2 . .	20·5	14·0	10·6	8·7
2 ,, ,, 4 . .	3·7	2·8	2·5	2·4

Synthetic amyl alcohol is not a solvent for cellulose esters or cumarone, but it dissolves ester gum, elemi, mastic, sandarac, kauri, shellac, and is miscible with castor and linseed oils and with hydrocarbons ; it partly dissolves dammar.

Fermentation of fusel oil amyl alcohol is available in several grades.

The pure quality of commerce answers to the following specification : S.G. at 15°, ·815–·817. B.R. 128°–132°. F.P. 105°–115° F. (40°–46° C.). I.P. 116° F. (47° C.). Acidity 0·01% max. as acetic, clearly miscible with benzene in all proportions ; V.P. at 20° 9–10 mm. ; R.I. 1·39–1·40. Water dissolves 3% at 20°. M.P. –134° C. I.H. 120. S.H. ·57. Vis. 3·3. Cub. exp. ·00093.

A less pure technical quality, known as *anhydrous fusel oil*, has the following approximate characteristics : S.G. ·813–·817. B.R. 105°–132°. F.P. about 97° F. (36° C.). Clearly miscible with benzene in all proportions. This quality contains small quantities of *n*-propyl, isobutyl and *n*-hexyl alcohols with traces of pyridine, furfural and esters.

*A.S.T.M. Amyl Alcohol D*319–40 [19] has S.G. 812–820 at 20° acidity—none. Residue ·005% max. B.R. up to 118°, none ; 120°, 5% max. ; 125°, 50% max. ; 130°, 85% max. Above 140°, none. Miscible with 19 vols of gasoline at 20°.

Fermentation amyl alcohol is a solvent for soft copals, ester gum, sandarac, shellac, benzyl abietate, cyclo-hexanone-formaldehyde and urea-formaldehyde resins. It is miscible with castor and linseed oils and with hydrocarbons. It is a moderately good solvent for ethyl cellulose, copal ester, mastic and cumarone, and has the property of rendering

glyceryl phthalate resins soluble in other solvents. It does not dissolve cellulose esters.

Isoamyl alcohol forms the following binary constant-boiling mixtures :—

Isoamyl alcohol	97·5%.	Isoamyl acetate 2·5%.	B.P. 131·3°
,,	26%.	Isoamyl formate 74%.	,, 123·6°
,,	60%.	*o*-Xylene 40%.	,, 128·0°
,,	53%.	*m*-Xylene 47%.	,, 127·0°
,,	51%.	*p*-Xylene 49%.	,, 126·8°
,,	49%.	Ethyl benzene 51%.	,, 125·9°
,,	19%.	Tetrachlorethylene 81%.	,, 116·0°
,,	36%.	Chlorbenzene 64%.	,, 124·3°
,,	19%.	Epichlorhydrine 81%.	,, 115·4°

The following ternary mixtures are known : Isoamyl alcohol 19·6% ; isoamyl formate 48% ; water, 32·4% ; B.P. 89·8°. Isoamyl alcohol, 31·2% ; isoamyl acetate, 24% ; water, 44·8% ; B.P. 93·6°.

Another form of synthetic amyl alcohol consists of the secondary alcohols obtained by hydrogenating the higher ketones of ketone or acetone oils (*q.v.*)

The higher ketones, on hydrogenation, give rise to secondary alcohols, the acetates of which have solvent properties similar to the primary alcoholic acetates, butyl and amyl acetates ; hexanol 2 and 2 methyl pentanol 4 have also been produced from olefines ; the boiling-points of those of greatest importance are :—

	Alcohol.	Acetate.
Secondary butyl alcohol . .	100° C.	112° C.
Pentanol 2	119° C.	134° C.
Pentanol 3	114° C.	132° C.
Hexanol 2	139° C.	153° C.
Hexanol 3	134° C.	150° C.
2 Methyl pentanol 4 . .	130° C.	148° C.

Secondary butyl alcohol is dealt with separately.

2 *Methyl pentanol* 4 is available commercially [24] and has B.R. 125°–131°. S.G. ·807. F.P. 46° C. Its *acetate* has B.R. 136°–146°. S.G. ·856. F.P. 45° C. Dil. rat. toluene 1·8, gasoline 1·1. Water dissolves ·8%.

It has also been proposed to manufacture amyl alcohol and its homologues from the olefines resulting from the cracking

of petroleum by absorption in sulphuric acid and hydrolysis of the acid sulphate thus formed.[25] Thus olefine gases are first passed through 75 to 85% sulphuric acid, in order to absorb butylene and amylene, and then through 100% acid to absorb propylene and ethylene, a series of towers being employed. The solutions, on steam distillation, yield the corresponding alcohols (*cf.* Isopropyl alcohol). The acetates, or other esters, may be obtained directly by treating the alkyl sulphate solutions with calcium or sodium acetate, or with the free fatty acid.[26] These methods do not yet appear to have attained industrial importance as regards amyl alcohol, although iso-propyl alcohol and secondary butyl alcohol are produced in large quantities by this means (*q.v.*).

Benzyl Alcohol. $C_6H_5 . CH_2 . OH$.

Benzyl alcohol is a widely-used high-boiling solvent which is valued on account of its plasticising effect, although this is not permanent. It is particularly useful as a medium in which to grind pigments intended for incorporation in a lacquer, and also for retarding the rate of evaporation of the solvent mixture; it tends to prevent the settlement of pigments.

It is manufactured chiefly by the alkaline hydrolysis of benzyl chloride under carefully regulated conditions. It is a neutral, stable, colourless and almost odourless liquid, and possesses exceptional solvent powers.

B.E.S.A. Specification 3*D*7.[11]—Colourless, anhydrous. containing a minimum of 97% of benzyl alcohol. S.G. 1·050–1·055. B.R. 95% between 200°–210°. B.P. min. 200°. Residue 1·0% max. Acidity 0·1% max. as benzoic, free from hydrochloric acid. Chlorine 0·05% max. Benzyl alcohol is soluble in water to the extent of 3 to 4% and dissolves about 8% of water at 20° C. R.I. 1·538–1·541. B.P. (pure) 205° C. M.P. –15° C. F.P. about 205° F. (96° C.). L.H. 111. S.H. ·54. Dielec. const. 13. Cub. exp. ·00073. Vis. 5·6. Chief impurities: benzaldehyde, chloro-toluene, di-benzyl ether, di-benzyl, benzyl chloride. It is a solvent for cellulose acetate, for ethyl and di-benzyl cellulose, ester gum, copal ester, glyceryl phthalate resin, cumarone, benzyl abietate, mastic, shellac, linoxyn, polystyrol. It is miscible with linseed and castor oils, and with aromatic hydrocarbons, but

not with the paraffins or water. Benzyl alcohol has a limited solvent action on cellulose nitrate and sulphur.

Diacetone Alcohol. $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C(OH) . CH_2 . CO . CH_3$

Diacetone alcohol, diacetone, or 4-hydroxy-4-methyl pentanone 2, is a ketol or ketonic alcohol the value of which has not been sufficiently appreciated. It is manufactured from acetone by condensation by means of alkalis and, when pure, is an odourless, colourless liquid. Technical qualities contain small quantities of acetone and occasionally also mesityl oxide, a dehydration product; it is to this last impurity that any offensive odour is due.

British Standard Specification No. 549—1934.[11]—S.G. ·937–·943 (·935–·941 at 20°). F.P. 40° C. min. (104° F.). B.R. up to 160°, 5% max., 160°–170°, 92% min.; acidity ·025% max., miscible in all proportions with water and petroleum ether.

It should be noted that diacetone alcohol slowly decomposes on heating and also on long storage, producing acetone; for this reason the figures given above for the boiling range and flash point may not be obtained; the purest material obtainable has the following characteristics: S.G. ·942. B.P. 164°. F.P. 55° C. (122° F.). M.P. −55° C. V.P. 9 mm. at 20° C. R.I. 1·424. Dil. rat. benzol 3·0, toluene 3·1, butanol 7·8. Cub. exp. ·00099.

Diacetone alcohol is a good solvent for both cellulose nitrate and acetate, also for colophony, bitumen tars, bakelite, glyceryl phthalate resin, polyvinyl chloride, shellac, benzyl-abietate kauri, manila, mastic, sandarac, and copals. It has moderate solvent properties for cellulose ethers, ester gum, cumarone, linseed oil, zanzibar, elemi, guaiac. It will not dissolve rubber or copal ester, and is not compatible with high-boiling paraffin hydrocarbons. Standard dilution ratio with toluene, 3 to 3·5.

Diacetone alcohol is of particular value for cellulose acetate lacquers, since, although a "high boiler," it does not remain in the film on evaporation for an undue length of time, as is the case with such high-boiling solvents as cyclohexanol and benzyl alcohol. It gives hard films, having a brilliant gloss, and it is particularly suitable for brushing lacquers destined

for use in interiors where odour is objectionable ; it is itself non-toxic.

Diacetone alcohol methyl ether, or 4-methoxy 4-methyl pentanone 2 is produced by condensing mesityl oxide with methyl alcohol.[27]. It is a liquid boiling 154°–158°.

Di-ethyl Ether. $C_2H_5 . O . C_2H_5$

Ether is not of itself a solvent for cellulose nitrate, but in admixture with alcohol it has found very extensive application in the manufacture of celluloid. The addition of quite a small proportion of alcohol imparts very powerful solvent properties for cellulose nitrate of high nitrogen content. Ether is not a solvent for cellulose acetate or cellulose ethers.

Ether is produced industrially by the well-known method of treating alcohol with sulphuric acid ; hence the name sometimes given to it—sulphuric ether—and from ethylene obtained during the distillation of petroleum ; also by passing alcohol vapour over activated hydrosilicates at high temperature.[28]

Ether is available in several qualities, the variations being largely due to the presence of alcohol, water and of the methylating agent in the alcohol used, other impurities which occur are acetaldehyde, vinyl alcohol, acetone, acetic acid and the explosive peroxide.

Characteristics : Pure Ether.—S.G. ·7199. B.P. 34·6°. M.P. −117°. F.P. −41° C. (−40° F.). Auto-ignition temp. 186° C. R.I. 1·356. S.H. ·538. L.H. 86. Vis. ·34. Elec. cond. $3·7 \times 10^{-13}$. Dielec. const. 4·4. Dissolves about 2% of water at 20°. Water dissolves 6·5 to 7% at 20°.

British Standard Technical Ether.—S.G. ·725 max. B.R. 95% below 36°. Residue ·005% max. Acidity ·002% max. as sulphuric acid ; completely miscible with benzene in all proportions.

Ether forms a constant-boiling mixture with ethyl alcohol, boiling at 74·8° and containing 40% of ether.

Ether is a very dangerous substance to handle. It is highly narcotic, and large doses readily lead to death ; it forms explosive peroxides and is exceedingly inflammable, and forms mixtures with air which can explode with great violence. The explosive limits (see p. 48) lie between 35 gm. and 200 gm. per cubic metre of air with a maximum explosivity at about 120 gm. Ether very readily acquires high static charges

of electricity which may give rise to sparks resulting in the ignition of the ether ; for this reason it is advisable to " earth " the contents of glass vessels from which any large quantity of ether is to be poured.

Di-Iso-Propyl Ether $C_3H_7 . O . C_3H_7$

Di-iso-propyl ether is used industrially for extractions at low temperatures. It is an exceedingly dangerous substance as it forms unstable peroxides, on contact with air, which explode with great violence when heated ; [29] this tendency can be limited by adding small proportions of stabilisers such as catechol, hydroquinone, aqueous sulphites or metallic copper.

Characteristics : S.G. ·730 B.P. 68° F.P. –7° F. (–22° C.). R.I. 1·37. S. ten 32. Vis. ·38 at 25°. S.H. ·526 . M.P. –60° C. V.P. 158. Water dissolves ·65% at 20°.

It forms a binary azeotrope with 14% of isopropanol B.P. 66·2°. It is a moderate solvent for cellulose nitrate when mixed with alcohol, for ethyl cellulose and for oils and some resins. Narcotic but non-toxic.

Di-*n*-Butyl Ether $C_4H_9 . O . C_4H_9$

This is a solvent for fats, oils, ester gum, rosin, dammar, but not for cellulose esters.

S.G. ·756–·772. B.P. 142°. M.P. –95°. V.P. 5. F.P. 25° C. Vis. ·32. Immiscible with water.

It forms explosive peroxides [29] similar to those mentioned above and has a mild odour.

Methylal. $CH_3 . O . CH_2 . O . CH_3$

Methylal, or formaldehyde di-methyl acetal, is a di-ether which, in the presence of alcohols, dissolves cellulose nitrate. It is a powerful narcotic.

Characteristics : B.P. 42°, M.P. –104°, S.G. ·86. S.H. 90. L.H. ·52. Water dissolves about 33%. Methylal is not widely used.

Acetal. $CH_3CH_2\begin{cases} O . C_2H_5 \\ O . C_2H_5 \end{cases}$

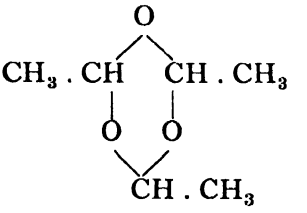
Acetal, or acetaldehyde di-ethyl acetal, does not dissolve cellulose acetate and is but a poor solvent for cellulose nitrate, but the admixture of anhydrous alcohol greatly increases its solvent power.

Characteristics : B.P. 102°. S.G. at 20°, ·82. L.H. 66. S.H. ·52. R.I. 1·38. Water dissolves about 5%.

Acetal forms a constant-boiling mixture with 67% of ethyl alcohol boiling at 79°.

Acetal solvent [30] consists of a mixture of acetal and alcohol which dissolves cellulose nitrate, kauri, manila and other resins. It has B.R. 75°–85° (90%). S.G. ·82. F.P. 38° F. Acidity ·01% max.

Paraldehyde.



Paraldehyde is a medium boiling solvent [31] for colophony and cumarone, it partly dissolves ester gum, dewaxed dammar and copals and is a latent solvent for cellulose nitrate ; its solvent power for the latter is activated by the addition of non-solvents such as alcohol and by solvents such as acetone ; its precipitating effect and evaporation rate are about one half that of toluene.

Paraldehyde is a powerful narcotic but is believed not to be definitely toxic, it possesses a somewhat choking odour. It slowly decomposes to acetaldehyde, and its flashpoint lowers and its acetic acid content rises in consequence.

It has sp. gr. ·998. R.I. 1·405. F.P. 81° F. (27° C.). M.P. 12°. B.P. 124°. Water dissolves 12%. Vis. 1·2.

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CHAPTER III

KETONES

Acetone. $CH_3 . CO . CH_3$

ACETONE or dimethyl ketone is one of the most widely used of the industrial solvents on account of its low cost, high solvent powers and comparative lack of toxicity. Its principal uses are as a low-boiling solvent for cellulose acetate and nitrate lacquers, as a medium for preparing acetate silk, for artificial leather manufacture, for dewaxing lubricating oils, for the manufacture of cordite explosive, photographic films, safety glass and for dissolving acetylene.

Acetone is or has been manufactured by a number of methods, but until recent years it was obtained solely from the distillation of wood or by the dry distillation of acetate of lime [1, 2] resulting therefrom. Much of the acetone now available is produced along with *n*-butyl alcohol by the fermentation of carbohydrate materials [1, 3, 4] while small amounts have been produced by the fermentation of the giant seaweed which grows along the Pacific Coast of North America, whereby acetic acid mixed with higher homologues is obtained,[5] the calcium salts of which yield the corresponding ketones on dry distillation. Large quantities of acetone were made during the period of the 1914 War by the direct catalytic treatment of acetic acid vapour with solid bases such as lime, baryta or magnesia,[6] while a still more modern process consists in the high temperature catalytic treatment of mixture of acetylene and steam. Acetone is now mainly produced by the fermentation method mentioned above, by the dehydrogenation of isopropyl alcohol [7] and by the treatment of ethyl alcohol vapour and steam at high temperature with catalysts such as the oxides of iron, copper or manganese.

Characteristics : The purest acetone has the following properties : S.G. at 20°, ·7912. R.I. 1·3599. Vis. ·32. B.P. 56·3. M.P. —94·9. V.P. at 20°, 180 mm. F.P. 2° F. (–16·7° C.). L.H. 122. S.H. ·52. H.C. 7373. Cub. exp. ·00149. S. ten. 24. Elec. cond. $5·5 \times 10^{-8}$. Dielec. const. 21. Dil. rat., benzene 5·2, toluene 4·5, butanol 7·0.

British Standard Acetone No. 509—1933 S.G. ·796–·798.

B.R. 55·5°–56·5° (95%). Acidity ·002% max. as acetic acid. Alkalinity to methyl red—*nil*. Residue ·005% max. Withstands permanganate test for thirty minutes minimum. Clearly miscible with water and with carbon disulphide in all proportions.

Cordite acetone must answer to the following specification : S.G. at 15° not over ·800. Free from colour, clearly miscible in all proportions with water. Acidity 0·002% max. as CO_2. Fixed acidity, nil. Aldehydes or other reducing substances, 1 part per thousand maximum. Must withstand the permanganate test for at least thirty minutes (viz., 1 c.c. of a 0·1% solution of $KMnO_4$ added to 100 c.c. of acetone kept at 15° C. in the dark, the colour to persist for at least thirty minutes).

U.S.P. standards require : S.G. ·792–·799 at 20° C. ; 99–100% di-methyl ketone. Acidity 0·002% max. as CO_2. Water white and water free. B.R. 56°–47°. No residue on evaporation. Clearly miscible with water. To stand the permanganate test for at least five hours.

A.S.T.M.[9] *Specification D*329–33 requires S.G. ·791–·799 at 20° ; 98% min. di-methyl ketone. B.R. below 55°, none ; above 57·5°, none. Non-volatile matter ·005% max. w/v. Acidity ·002%, max. as CO_2. Not alkaline to *p*-nitrophenol. To withstand permanganate test for at least 30 mins. Miscible with water and with gasoline in all proportions. Water white.

Acetone is one of the most powerful solvents known. It dissolves cellulose acetate, benzoate, nitrate, accto-nitrate, ethyl cellulose, glyceryl phthalate resins, thiourea resin, croton-aldehyde resin, cyclohexanone-formaldehyde resin, benzyl abietate, vinyl resin, plextol, ester gum, copal ester, and Albertol 82G. It is miscible with castor, linseed, china-wood, cotton seed, fish, olive, palm, peanut and polymerised oils, and with most hydrocarbons. Its solvent action on rubber varies widely with the rubber.[10] Acetone causes benzyl cellulose to swell.

The solubilities of natural resins, waxes and pitches are approximately as follows :—

Solubility 90% *or more*. Beeswax, candelilla wax, elemi, dammar, Japan wax, soft manila, mastic, pontianac, rosin, sandarac, shellac.

Solubility 50–90%. Copal, kauri, montan wax, ozokerite refined coal-tar pitch.

Solubility 20–50%. Carnauba wax, Congo copal, gilsonite, hard manila, refined Trinidad pitch.

Solubility below 20%. Arabic, tragacanth, Syrian asphalt.

Acetone forms the following azeotropic mixtures :—

Acetone 86·5%.	Methyl alcohol 13·5%.	B.P. 55·95° C.
,, 34%.	Carbon disulphide 66%.	,, 29·25° C.
,, 20%.	Chloroform 80%.	,, 64·7° C.

the last mixture has a boiling-point higher than that of either of its components.

S.G. at 20° of acetone-water mixtures [12] :—

Per cent Acetone	S.G.	Per cent Acetone.	S.G.
10	·986	60	·900
20	·974	70	·877
30	·958	80	·852
40	·942	90	·825
50	·921	100	·795

"Methyl Acetone" and "Wood Spirit"

In the manufacture of acetone and methyl alcohol from wood, fractions are obtained containing methyl acetate and other substances which cannot economically be separated one from another ; these fractions have excellent solvent properties and are recognised articles of commerce, but they vary somewhat widely in composition. The composition of "Methyl acetone" varies usually between the following limits : Methyl acetate, 20–30% ; acetone, 35–60% ; methyl alcohol, 20–40%.

The *B.E.S.A. Specification* 2D1,[8] is as follows : Almost colourless ; anhydrous. S.G. ·830. B.R. 50°–70° C. Acidity 0·02% max. Acetone 45–60%. F.P. below 32° F. Clearly miscible with water in all proportions.

Wood spirit, known also as wood naphtha and as wood alcohol, contains about 80% of methyl alcohol and varying quantities of acetone, methyl acetate, acetal, allyl alcohol, acetaldehyde and methylamine.

Methyl acetone is an excellent solvent for cellulose acetate and nitrate. The B.E.S.A.[8] method for determining the solvent power of methyl acetone for cellulose acetate is as follows : Six grams of cellulose acetate (Air Board Specification D6) are dissolved in 100 c.c. of pure dry acetone. A solution of similar concentration is made, using the methyl acetone under examination. A measured volume of each solution is taken and alcohol (Specification D9) is slowly

added from a burette, while shaking and carefully keeping the mixtures at 25° C. by means of a constant temperature bath. The alcohol is added until a faint opalescence appears in each solution. The ratio between the quantities of alcohol required for each solution, reckoned as a percentage of that required for the pure acetone solution, represents the solvent power of the material under consideration. The B.E.S.A. recognises three grades, viz., 65%, 50% and 30%, compared with acetone 100%.

Methyl acetone is a solvent for ester gum, benzyl abietate, glyceryl phthalate resin, and is miscible with castor and linseed oils, hydrocarbons, and water.

Wood spirit is an exceedingly rapid solvent for cellulose nitrate; it also dissolves cellulose acetate, ester gum, benzyl abietate, glyceryl phthalate resin, cumarone, castor and linseed oils. It partially dissolves shellac, mastic, copal, and is miscible with hydrocarbons and with water.

"Methone" is a form of methyl acetone in which the alcohols are replaced by esters, thus enhancing its solvent properties considerably.

Methyl Ethyl Ketone. $CH_3 . CO . C_2H_5$

Methyl ethyl ketone, or butanone, known commercially as M.E.K., is obtained along with acetone and several other homologous ketones by the destructive distillation of wood, also by the dehydrogenation of secondary butyl alcohol.

The formation of higher ketones from lower ketones and alcohols has been accomplished by passing the appropriate mixture with hydrogen over aluminium oxide catalyst at temperatures ranging from 150°–400°; thus acetone and methyl alcohol at 230° yield methyl ethyl ketone, di-ethyl ketone and higher ketones as the main products.

The composition of technical M.E.K. varies somewhat, but the *B.E.S.A.* $3D1^{8}$ requires S.G. ·810–·815. B.R. 95% between 68°–85°. Acidity or alkalinity 0·01% max. as acetic acid. Residue 0·01% max. Higher ketones 5% max. by vol. Acetone and alcohol 7·5% max. by vol. No opalescence with an equal volume of carbon disulphide. Colourless.

*A.S.T.M.–D*268—33 requires B.R. 79°–80·5° C.

This quality is a good solvent for cellulose nitrate and for ethyl cellulose, kauri, manila, pontianac, colophony, ester gum, benzyl abietate, plextol, glyceryl phthalate resin, vinyl

resin, cumarone, dewaxed dammar. Its solvent power for cellulose acetate varies with variations in the latter, but in general M.E.K. is not a good solvent for cellulose acetate. It does not dissolve carnauba, beeswax, ceresine or paraffin wax. It is miscible with castor and linseed oils and with hydrocarbons. Flash-point, below 0° C.

The following azeotropic mixtures are known [11] :—

Methyl ethyl ketone 88·6%.	Water 11·4%.	B.P. 77·6° C.
,, ,, 15%.	Carbon disulphide 85%.	,, 45·8° C.
,, ,, 29%.	Carbon tetrachloride 71%.	,, 73·8° C.
,, ,, 45%.	Benzene 55%.	,, 78·5° C.
,, ,, 69%.	Methyl alcohol 31%.	,, 64·1° C.
,, ,, 66%.	Ethyl alcohol 34%.	,, 74·8° C.
,, ,, 68%.	Isopropyl alcohol 32%.	,, 77·5° C.
,, ,, 52%.	Methyl propionate 48%.	,, 79·25° C.
,, ,, 55%.	Propyl formate 45%.	,, 79·45° C.
,, ,, 22%.	Ethyl acetate 78%.	,, 76·7° C.

Pure methyl ethyl ketone has R.I. 1·379, B.P. 79·6° C., M.P. –86° ; F.P. 19° F. (–7° C.) ; L.H. 104, S.H. ·55, V.P. at 20°, 77·5, S.G. at 20°, ·8050, Cub. exp. ·0013, Vis 40. S. ten. 25. Dil. rat. 4·5. It will dissolve about 12% of its weight of water, and water will dissolve about 23% of its weight of the ketone at 20° C.[11 15].

Butyrone. $C_3H_7 . CO . C_3H_7$

Butyrone, heptanone 4, or di-*n*-propyl ketone is manufactured from wood, which is saccharified and then fermented in the presence of chalk, whereby impure calcium butyrate is produced. Calcium butyrate on dry distillation yields butyrone. The wide boiling range of the technical product is accounted for by the fact that aliphatic acids other than butyric are also produced ; a variety of ketones consequently arises on distilling the calcium salt.

Butyrone is a poor solvent for both cellulose acetate and for nitrate ; it dissolves caoutchouc, ester gum, cumarone, linseed and castor oils, glyceryl phthalate and other resins. It is miscible with hydrocarbons. It possesses a rather sweet odour resembling pineapples, and is non-toxic at normal concentrations.

Technical butyrone has S.G. 820 ; B.R. 137°–144° ; F.P. about 49° C. ; Dil. rat. toluene 3·1.

Pure butyrone has B.P. 143·5° ; S.G. at 20°, ·823 ; M.P. –32° ; R.I. 1·41. Vis. ·685 at 25°.

Higher Ketones

Several ketones of higher molecular weight are being produced in limited quantities and in varying degrees of purity.[13] They are, in general, good solvents for cellulose nitrate, but have little or no action on cellulose acetate. They dissolve ethyl cellulose, ester gum, colophony, manila, pontianac, glyptal, cumarone and vinyl acetate resin. The following are the most important :—

Di-ethyl ketone, known also as amyl ketone, pentanone 3, propionone and di-methyl acetone. The pure substance has S.G. ·818 ; B.P. 101°. Cub. exp. ·00113. Vis. 47. It dissolves 2% of water at 20°. The commercial product is a colourless liquid having a fruity camphoraceous odour, and consists of a mixture of di-ethyl ketone and methyl *n*-propyl ketone with about 2% of non-ketonic impurities. It has S.G. at 20°, ·807—·811 ; B.R. 90% between 100°–105°.

Methyl n-propyl ketone, or pentanone 2, has S.G. ·812. B.P. 102°. R.I. 1·3895. V.P. 30 mm. at 20°. F.P. 45° F. (7° C.). L.H. 91. M.P. –83°. Vis. ·5. Dissolves 3·6% of water at 25°. Water dissolves 6% at 25°. Dil. rat. toluene 4·4.

Methyl n-butyl ketone, or hexanone 2, has S.G. ·817. B.P. 127°. R.I. 1·4024. V.P. 10 mm. at 20°. F.P. 73° F. (23° C.). L.H. 83. S.H. ·553. Vis. ·63. Dissolves 3·7% of water at 25°. Water dissolves 3 to 4% at 25°. Dil. rat. toluene 4·1. Cub. exp. ·001.

Methyl isobutyl ketone, or 2-methyl pentanone 4, known industrially as hexone, is a medium boiling solvent for nitrocellulose. When mixed with ethylene dichloride it dissolves cellulose acetate. S.G. 20° ·800. B.R. 116° ; dil rat. toluene 4·0. F.P. 23° C. V.P. 15. Dissolves 2·8 of water at 20° ; water dissolves 1·9% at 20° ; vis. ·58. Methyl isobutyl ketone is a solvent for dammar estergum, elemi, mastic, sandarac, ethyl cellulose, benzyl cellulose, cellulose nitrate ; it is miscible with mineral and vegetable oils. It partly dissolves kauri, zanzibar, pontianac, manila, beeswax, paraffin wax and blown oils ; it is a non-solvent for shellac, tragacanth and carnauba wax.

Methyl n-amyl ketone, or heptanone 2, has S.G. ·820. B.P. 150°. R.I. 1·411. V.P. 3 mm. at 20°. F.P. 106° F. (41° C.). L.H. 83. Vis. ·81. Dissolves 2% of water at 25°. Water dissolves 2% at 25°. Dil. rat. toluene 3·9.

This ketone is available technically with the following

characteristics: S.G. at 20° ·816–·821. B.R. 147°–154° Acidity ·05% max. as acetic acid. Dil. rat. toluene 3·9.

Mesityl Oxide. $(CH_3)_2 > C : CH . CO . CH_3$

This is an unsaturated ketone obtained by dehydrating diacetone alcohol, or prepared direct from acetone by means of anhydrous alkalis, such as lime, or dehydrating agents, such as zinc chloride or hydrochloric acid gas. It has a rather strong odour suggestive of mice and peppermint, which precludes its extensive use. Mesityl oxide occurs in acetone oils along with a further condensation product of acetone, phorone, $(CH_3)_2 : C : CH . CO . CH : C : (CH_3)_2$. B.P. 197°.

Mesityl oxide is a solvent for low viscosity cellulose acetate and nitrate and yields tough, transparent and glossy films. It dissolves vinyl resins and synthetic rubber, ethyl cellulose and most oils. Were it not for its disagreeable odour, it would undoubtedly be used extensively as a solvent for cellulose acetate. It has been recommended as a paint-stripper.[14]

Characteristics: S.G. ·855–·865 (·853–·863 at 20°). R.I. 1·44–1·45. Dissolves 3% of water at 20°. Water dissolves 3% at 20°. F.P. 78° F. (26° C.). B.R. 110°–140°. 60% min. between 126°–131°. The pure material has: B.P. 129°; M.P. –59° C.; L.H. 86; Vis. 87 at 25°; R.I. 1·444; Dil. rat. toluene 3·8; Cub. exp. ·0011.

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CHAPTER IV

ESTERS

Methyl Acetate. $CH_3 . COO . CH_3$

THIS ester is similar to acetone in character, the boiling-points of the two liquids being the same and their solvent powers comparable. Methyl acetate is not widely used, since it readily becomes acid on contact with water, and the fact that its parent alcohol—methyl alcohol—is poisonous also militates against its industrial employment. It is chiefly used to replace acetone when expediency demands.

Pure methyl acetate has S.G. ·933 ; B.P. 57° ; M.P. –98° ; R.I. 1·362 ; F.P. –13° C. ; S.H. ·50 ; L.H. ·98 ; Vis. ·38. Elec. cond. $1·92 \times 10^{-4}$. Dielec. const. 8·02. Cub. exp. ·00134.

The B.E.S.A. Specification, *D*13, is as follows : S.G. ·92–·94. B.R. 55°–60°. Esters 80% min. Acidity 0·1% max. Residue 0·01% max. It should be clearly miscible in all proportions with benzene and with water.

The following azeotropic mixtures are of interest :—

Methyl acetate	81·%	Methyl alcohol 19%.	B.P. 54·0° C.
,,	30%.	Carbon disulphide 70%.	,, 40·2° C.
,,	45%.	Acetone 55%.	,, 56·1° C.
,,	30%.	*Iso*-propyl alcohol 70%.	,, 77·3° C.

It is a good solvent for cellulose nitrate and acetate, for ester gum, colophony, kauri, manila, sandarac, plextol, benzyl abietate, glyceryl phthalate resin, and is miscible with castor and linseed oils and with hydrocarbons. It is a solvent for ethyl cellulose [1] when mixed with other substances such as camphor, triphenyl phosphate, cyclohexanol, ethyl benzene, acetophenone, butyl tartrate, cyclohexanone, dibenzylamine, dimethyl aniline, ethyl benzyl aniline, diphenylmethane, monochloro-naphthalene.

It does not dissolve copal ester gum, shellac, dammar, elemi or cumarone. It is miscible with water ; at 20° C. water will dissolve 24·35% by weight of methyl acetate. It is made by esterification, in the liquid phase, or by passing the mixed vapours of methyl alcohol and acetic acid over heated catalysts.[2]

Ethyl Acetate. $CH_3 . COO . C_2H_5$

The use of this solvent for the manufacture of cellulose nitrate lacquers is becoming rapidly more widespread, as it is undoubtedly the best of the low-boiling solvents. It has considerable advantages over acetone; its boiling-point is higher and its evaporation rate about one half that of acetone, and it is therefore less likely to cause chilling. Its dilution ratios for cellulose nitrate solutions against dilution with alcohols and paraffins are larger than those of acetone, although smaller against aromatic hydrocarbons. Pure ethyl acetate is not a solvent for cellulose acetate, 5 to 30% of uncombined alcohol being necessary to effect solution, and for this reason ethyl acetate containing up to 15% of dry alcohol is frequently employed for both cellulose acetate and nitrate, the presence of free alcohol also improving its solvent powers for the nitrate. Solutions of cellulose nitrate in ethyl acetate have viscosities about one-third of solutions of corresponding concentration in butyl acetate, and one-fifth of those in amyl acetate; such solutions have tolerances for dilution with butyl alcohol, toluene or xylene approaching those in ethyl lactate.

Ethyl acetate is mainly manufactured by direct continuous esterification; it is also made by the catalytic condensation of acetaldehyde by means of alkoxides.

Ethyl acetate is available commercially in several grades.

British Standard Ethyl Acetate No. 553—1934, has the following characteristics: S.G. ·906–·909 (·901–·904 at 20°). Esters 96% min. B.R. 95% between 74° and 69°. Residue ·01% max. Acidity ·01% max. Clearly miscible with 10 volumes of carbon disulphide.

*A.S.T.M. Ethyl Acetate D*302–33 [4] has S.G. ·883–·888 at 20°. Esters 85–88%. Acidity ·02%. B.R. up to 70°, none; 72°–10% max.; above 80°, none. Residue ·005% max. Miscible with 10 vols. of gasoline at 20°.

Technical 99–100% *Ethyl Acetate* is the product most widely used in Britain, and has S.G. ·906–·907. Esters 99–100%. Acidity ·01% max. Residue ·01% max. B.R. 76°–78° (95%). Clearly miscible with carbon disulphide in all proportions.

Pure ethyl acetate has the following characteristics: S.G. ·9066. B.P. 77·15°. V.P. at 20° 73 mm. F.P. −4° C. M.P. −83·6°. Cub. exp. ·0013. L.H. ·87. S.H. ·48. R.I.

1·373. Vis. ·45. Water dissolves 8·6% of ethyl acetate at 20° C. (another authority quotes 6·44%). Dil. rat. benzol 3·4, toluene 3·4, butanols 8·4. Elec. cond. $<1\times10^{-9}$. Dielec. const. 6·11.

Ethyl acetate produced in the United States is denatured with $\frac{1}{8}$% of a petroleum product such as "Calol Ethatate" produced by the Standard Oil Co. This denaturant is a by-product of petroleum cracking, and has a strong, gas-like, coal-oil odour. Its vapour pressure is such that it does not interfere with the use of ethyl acetate in lacquers.

The following azeotropic mixtures are known :—

Ethyl acetate 69·4%.	Ethyl alcohol 30·6%.	B.P. 71·8°.
,, 77%.	Isopropyl alcohol 23%.	,, 74·8°.
,, 3%.	Carbon disulphide 97%.	,, 46·1°.
,, 43%.	Carbon tetrachloride 57%.	,, 74·7°

and a ternary mixture consisting of ethyl acetate 83·2%, ethyl alcohol 9%, water 7·8%, boiling at 70·3°. It forms a pseudo-azeotrope with 8·2% of water boiling at 70·45°.

Ethyl acetate is a good solvent for cellulose nitrate, rubber chloride, ethyl cellulose, colophony, ester gum, benzyl abietate, vinyl resin, plextol, cyclohexanone-formaldehyde resin, cumarone, mastic, thus, albertols, polystyrene and poly-vinyl acetate. It is miscible with castor and linseed oils and with hydrocarbons. In the presence of up to 33% of alcohol it dissolves cellulose acetate, glyceryl phthalate resins, elemi, dammar. Ethyl acetate partially dissolves sandarac, kauri, manila and shellac. It does not dissolve hard copals or congo.

n-Propyl Acetate. $CH_3 . COO . C_3H_7$

So-called "technical" amyl acetate consists of *n*-propyl acetate along with other homologues arising from the esterification of fusel oil. Propyl acetate is seldom found in a state of purity. As is to be expected, its properties are similar to and intermediate between those of ethyl and *n*-butyl acetates.

It is a good solvent for cellulose nitrate, ester gum, sandarac, colophony, manila, cumarone, mastic, benzyl abietate, but not for cellulose acetate or hard copals. It is miscible with castor and linseed oils and with hydrocarbons. It is partly miscible with water ; water dissolves 1·89% by weight at 20° C.

The following binary azeotropic mixtures are known :—

n-Propyl acetate 86%.	Water 14%.	B.P. 82·4°.
,, 60%.	*n*-Propyl alcohol 40%.	,, 94·2°.
,, 77%.	*Iso*-propyl alcohol 23%.	,, 74·8°.
,, 43%.	Carbon tetrachloride 57%.	,, 74·7°.

and a ternary mixture containing 19·5% of propyl alcohol 21% of water, B.P. 82·2°.

The pure ester boils at 101·6° and has S.G. ·897, M.P. —95°. L.H. 80. S.H. ·47. R.I. 1·384. F.P. 14°. Vis. ·58. Elec. cond. 2·2 × 10^{-4}. Dielec. const. 8·1. It is non-toxic and its odour is mild and pleasant.

Isopropyl Acetate. $CH_3 . COO . CH(CH_3)_2$

This ester is produced by esterifying iso-propyl alcohol (*q.v.*). It has also been made by treating liquefied propylene with a mixture of acetic and sulphuric acids and similar methods. It is similar in character to *n*-propyl acetate, and its properties are intermediate between those of ethyl and butyl acetate. Its evaporation rate is about one-third of that of ethyl acetate.

Technical Specification : S.G. ·865–·90. B.R. 82°–90°. Esters 85–100%. Acidity 0·02% max. as acetic acid max.·; clearly miscible with benzene in all proportions.

The pure ester has S.G. ·93. B.P. 88·8° C. F.P. about 8° C. M.P. –73°. R.I. 1·377, S.H. ·52. L.H. 78. Elec. cond. 5·7 × 10^{-7}. S. ten. 24·5. Vis. ·52. Water dissolves 3·1% by weight at 20°. It forms a binary mixture with isopropyl alcohol, boiling at 80·1° and containing 52·3% of the alcohol, and with 14% of water boiling at 82·4°.

It is a good solvent for cellulose nitrate, ester gum, cumarone, elemi, sandarac, mastic, kauri. It partly dissolves shellac, but will not dissolve cellulose acetate or hard copals. It is miscible with castor and linseed oils and with hydrocarbons.

***n*-Butyl Acetate.** $CH_3 . COO . CH_2 . CH_2 . CH_2 . CH_3$

This is the most widely used of all the solvents of cellulose nitrate. It is probably the best for cold lacquers and " cellulose paints," since its volatility is sufficiently high for it to leave the film readily and sufficiently low to render it an excellent blush preventive, especially in conjunction with

butyl alcohol; the mixture of the two effectively prevents chilling as well as gum and cotton blush.

Butyl acetate is non-toxic and has a less pronounced odour than amyl acetate; it gives solutions of cellulose nitrate of somewhat lower viscosity than the latter. It is a better solvent for phenol formaldehyde resins. In the presence of about 20% of butyl alcohol it is an excellent solvent for the less highly polymerised forms of glyceryl phthalate resin and also for shellac. It is a good solvent for ester gum, benzyl abietate, cumarone, colophony, vinyl resin, cyclohexanone-formaldehyde resin, gum camphor, dammar, elemi, mastic, kauri, pontianac, sandarac, manila, rubber chloride, gutta percha resin, plextol; it partly dissolves copal ester, calcium, zinc and manganese resinates, but is a non-solvent for cellulose acetate and hard copal. It is miscible with castor, linseed and other oils, also with hydrocarbons. Some cellulose ethers can be dissolved in butyl acetate, notably "medium viscosity" ethyl cellulose.

The British Standard Specification No. 551—1934 [3] is as follows: S.G. ·883–·886 (·879–·882 at 20°). B.R. 124–128°, 95 % min. Esters 97% min. Acidity ·01% max. Residue ·01% max.

Pure *n*-butyl acetate has B.P. 126·5°. M.P. –77°. R.I. 1·3948 at 25°. F.P. 78° F. (25° C.). L.H. 74. V.P. 22. Crit. tem. 306°. Dielec. const. 5. Cub. exp. ·00117. Vis. ·67 at 25°. Dil. rat., benzol 2·8, toluene 2·8, butanol 8·2.

*A.S.T.M. Specification D*303–40 [4] requires S.G. ·872–·878 at 20°. Esters 88–92%. Acidity ·03% max. Residue ·005% max. B.R. up to 110°, none; 120°, 15% max.; above 127°, 30% max.; above 145°, none.

The following constant-boiling mixtures are known ·—

n-Butyl acetate	71·3%.	Water 28·7%.	B.P. 90·2° C.
,,	27%.	*n*-Butyl alcohol 73%.	,, 116° C.
,,	60%.	*n*-Propyl alcohol 40%.	,, 94·2° C.
,,	48%.	*Iso*-propyl alcohol 52%.	,, 80·1° C.

A ternary mixture, consisting of *n*-butyl acetate 35·3%, *n*-butyl alcohol 27·4%, water 37·3%, boling at 89·4° C.

Butyl acetate dissolves water to the extent of 1·2% at 10° C., 1·28% at 15° C., 1·37% at 20° C., 1·55% at 30° C., by weight. Water dissolves 0·8% by weight of butyl acetate at 15° and 1·0% at 20°.

Secondary Butyl Acetate. $CH_3 . COO . CH\begin{<}{l}CH_3\\C_2H_5\end{>}$

Secondary butyl acetate is used to some extent in America and on the Continent, and it is made by the direct esterification of the corresponding alcohol. The technical product contains isomers and homologues.

Characteristics : S.G. ·861. B.R. 107°-114°. Esters 85% min. Acidity 0·02% max. Clearly miscible with benzene. Solubility in water 3%. Dissolves 2·5% of water at 25° C. B.P. 112°. R.I. at 20° 1·3915. Cub. exp. ·00113. It has the fruity odour common to this class of ester ; it is non-toxic. Its rate of evaporation is intermediate between that of isopropyl and *n*-butyl acetates. It forms a constant-boiling mixture with 86·3% of sec. butyl alcohol boiling at 99·6°, and with 17% of water boiling at 87·4°.

It is a solvent for cellulose nitrate, ester gum, mastic, kauri, cumarone, elemi, benzyl abietate, colophony, pontianac, manila, tar, asphalt. It partly dissolves shellac and dammar. It does not dissolve cellulose acetate. It is miscible with castor and linseed oils and with hydrocarbons.

Isobutyl Acetate. $CH_3 . COO . CH_2 . CH\begin{<}{l}CH_3\\CH_3\end{>}$

This ester occurs to a considerable extent in the so-called " technical " amyl acetate along with other homologues. It is seldom used in a state of purity. It is an excellent solvent, giving solutions of low viscosity, somewhat lower than those of *n*-butyl acetate ; these solutions, however, are somewhat prone to chilling, and the addition of amyl acetate is therefore desirable ; for this reason the technical amyl acetate referred to above is preferred. Isobutyl acetate is non-toxic and its odour is mild and pleasant.

The following are the characteristics of a good commercial quality : S.G. ·868-·875. B.R. 110°-118°. F.P. 18° C. R.I. about 1·392. Esters 95-100%. The pure ester has B.P. 116·1° V.P. at 20° 13 mm. L.H. 74. S.H. ·46. R.I. 1·39. Vis. ·7. Elec. cond. $2·55 \times 10^{-4}$. Dielec. const. 5·32.

The following constant-boiling mixtures are known :—

Iso-butyl acetate 71%.	Water 29%.		B.P. 90·2° C.
,, 55%.	*Iso*-butyl alcohol 45%.		,, 107·4° C.
,, 53%.	*n*-Butyl alcohol 47%.		,, 117·2° C.

A ternary mixture consisting of 46·5%, isobutyl acetate 23·1%, isobutyl alcohol and water 30·4%, boils at 86·8°.

It is a good solvent for cellulose nitrate, ester gum, colophony, sandarac, benzyl abietate, cumarone and mastic, and in the presence of alcohols for glyceryl phthalate resin. It is miscible with castor and linseed oils and with hydrocarbons and partly with water. It does not dissolve cellulose acetate, copals, or copal ester.

Amyl Acetate

Amyl acetate is the doyen of the cellulose nitrate solvents, and, in spite of the many new ones that have been introduced during the last decade, still remains without equal, with the possible exception of *n*-butyl acetate. Its one great disadvantage is its powerful, but harmless, " banana " or " pear drop " odour, which to some is objectionable ; its superiority over other solvents is, however, so marked that its odour is tolerated for the sake of its unique qualities.

It is made by the acetylation of amyl alcohol (*q.v.*), obtained either from fusel oil or by synthetical methods, and is available in various grades, depending on the presence or otherwise of homologous or isomeric alcohols.

British Standard Amyl Acetate No. 552—1934 [3] has : S.G ·872–·880 (·868–·876 at 20°). B.R. 120–145, 95% min. ; above 135°, 33% min. Esters 95% min. Acidity ·01% max. Clearly miscible with 10 vols. carbon disulphide. Residue ·01% max.

The A.S.T.M. specifications [4] are as follows : For amyl acetate from fusel oil D554–39 : S.G. ·860–·865 at 20°. Esters 85–88%. Acidity ·03% acetic max. Residue ·005% max. B.R., below 110°, none ; 120°, 15% max. ; 130°, 50% max. ; 140°, 60% min. Above 150°, none. Clearly miscible with 19 vols. gasoline at 20°.

For synthetic amyl acetate D318–39 : S.G. ·860–·870 at 20°. Esters 85–88%. Acidity ·03% acetic max. Residue ·005% max. B.R., below 126°, none ; 130°, 5% max. ; 135°, 25% max. ; 140°, 75% min. ; above 155°, none. Clearly miscible with gasoline at 20° in all proportions.

The purest technical material available has : S.G. ·876–·878. B.R. 138°–142°. Esters 98–100%.

Pure iso-amyl acetate has B.P. 139·5–140. L.H. 69. S.H. ·46. R.I. 1·40. F.P. 25° C. (77° F.). Vis. about ·87. Dielec. const. 4·81. Cub. exp. ·00119.

The technical grade consists of the acetic esters of all the higher alcohols occurring in fusel oil, namely: *n*-propyl, isobutyl, isoamyl, active amyl, *n*-hexyl, *n*-heptyl alcohols; all primary alcohols. Neither the primary alcohols, isopropyl or *n*-butyl, nor any secondary or tertiary alcohols, seem to occur in traceable quantities.[5] The "pure" grade consists almost entirely of isoamyl and active amyl acetates, the ratio being about four to one; the boiling-points of these two esters and of the alcohols themselves are so similar that it is not technically feasible to separate them.

There occurs in fusel oil a quantity of a high-boiling, evil-smelling substance of complex composition, which is highly deleterious to lacquer films, since it imparts its disagreeable odour to them, tends to cause them to turn brown with age, and also diminishes the toughness, strength and adhesion. Amyl acetate for lacquer work should evaporate completely, leaving no such evil-smelling residue.

The specific gravities and boiling-points of the acetates of the alcohols of fusel oil are as follows:—

Alcohol	S G at 15°.	B.P.
n-Propyl acetate	·897	101·6° C.
Isobutyl acetate	·875	116·3° C.
Isoamyl acetate	·876	138·8° C.
Active amyl acetate	·890	141·2° C.
n-Hexyl acetate	·890	169° C.
n-Heptyl acetate	·875	191·2° C.

Amyl acetate is a good solvent for cellulose nitrate, ethyl cellulose, ester gum, colophony, dammar, albertols, benzyl abietate, cyclohexanone-formaldehyde resin, vinyl resin, gutta percha resin, plextol, cumarone, mastic, copals, kauri, sandarac, zanzibar, elemi; it partly dissolves shellac, animi, olibanum, carnauba wax, copal ester, linoxyn; it does not dissolve cellulose acetate. It is miscible with castor, linseed and other varnish oils and with hydrocarbons. When mixed with alcohols it dissolves glyceryl phthalate resins and ethyl cellulose. Pure amyl acetate is soluble in water to the extent of 0·2% at ordinary temperatures, and will dissolve 1% of water at 24°. V.P. at 20° 4·5 mm. Isoamyl acetate forms a constant-boiling mixture with 97·5% of isoamyl alcohol boiling

at 131·3°, also with 45% of isobutyl alcohol boiling at 107·4° and with 86% of sec-butyl alcohol boiling at 99·6°.

" Synthetic amyl acetate," produced from petroleum, comes into the market under the trade name of " Pentacetate " [6] (*vide* Synthetic amyl alcohol). It consists of a mixture of five of the eight possible isomeric esters, together with small quantities of free alcohols. It complies with the following specification : S.G. at 20° ·860–·870. B.R. 126°–155° (viz., 100% above 126° ; 95% above 130° ; 75% above 135° ; and 25% above 140°). Ester-content above 85% as amyl acetate. Acidity 0·03% max.

Its solvent properties are similar to those of fusel-oil amyl acetate, and its tolerance for toluene is about the same as that of pure amyl acetate and secondary butyl acetate, but is not so high as that of *n*-butyl acetate or ethyl acetate. The viscosities of its solutions of cellulose nitrate are nearly identical with those of solutions in pure amyl acetate. Penta-acetate is stated to be slightly but not dangerously toxic. It forms a " constant-boiling mixture " with 33% of water, boiling at 92°–95° C. " Pentexel " [6] is a similar mixture of lower ester content.

sec-Amyl Acetate

Commercial products consisting mainly of the acetates of the secondary alcohols pentanol 2 and pentanol 3 are now available. They are produced by synthetical processes from petroleum distillates, and vary in quality as shown by the following figures :—

A.[7]—S.G. at 20° ·861–·865. Esters 89–93%. Acidity 0·02% max. Residue 0·005% max. B.R. 120°–140°, 95% between 120°–135°, 85% between 125°–135°.

B.[8]—S.G. at 20° ·863. Esters 85–88%. B.R. 128°–134°. R.I. 1·4021. Dissolves 0·8% of water at 25° C. Cub. exp. ·00108. F.P. 89° F.

It has a somewhat lower tolerance for dilution than fusel-oil amyl acetate, and its odour is slightly less provocative of coughing ; its solvent properties are similar.

Hexyl Acetates

A number of isomeric hexyl acetates are now available commercially ; these substances are similar to amyl acetate in character but of higher boiling range. They are solvents for cellulose nitrate, colophony, ester gum, dammar, kauri,

cumarone, manila, elemi, pontianac, pitch, tar, asphalt, but not for cellulose acetate or shellac. Their characteristics are as follows :—

4-Methyl pentanyl-acetate

S.G. ·856 at 20°. B.R. 136°–146° C. F.P. 45° C. (113° F.). Dil. rat. toluene 1·8, petroleum 1·1. R.I. 1·394. Vis. 2·2 at 25° C. Dissolves ·9% water at 20°. Water dissolves ·8% at 20°.

2-Ethyl butyl-acetate

S.G. ·875–·881 at 20°. B.R. 155°–164°. Esters 90% min. R.I. 1·410. Vis. 1·1 at 20°. F.P. 57° C. (134° F.). Water dissolves ·064% at 25° C. Dissolves ·57% of water at 20°. Dil. rat. toluene 1·5.

1-Methyl pentanyl acetate :

S.G. ·859–·866 at 20°. B.R. 132°–159°. Esters 85% min. Acidity ·03% max. R.I. 1·408.

Ethyl Formate. $H.COO.C_2H_5$

This is a highly volatile solvent, having a boiling-point similar to that of acetone ; it is only used when expediency demands. Its odour is less powerful than that of acetone, and it is non-toxic. It is not a stable ester ; it readily develops acidity in the presence of moisture, and it cannot therefore be recommended for metal lacquers.

Physical Characteristics : S.G. ·925–·930. B.R. 53°–57°. B.P. 54·3°. M.P. –80°. R.I. 1·360. F.P. –19° C. Clearly miscible with benzene. Soluble in 9 parts of water at 18° C. S.H. ·51. L. H. 97. Vis. ·39. Elec. cond. $2{\cdot}63 \times 10^{-5}$ Dielec. const. 9·1.

The following azeotropic mixtures are known :—

Ethyl formate 84%.	Methyl alcohol 16%.	B.P. 51°.
,, 37%.	Carbon disulphide 63%.	,, 39·4°.

It is a rapid solvent for cellulose nitrate and acetate, giving solutions of low viscosity, which, however, are highly prone to chilling.

***n*-Butyl Formate.** $H.COO.CH_2.CH_2.CH_2.CH_3$

Butyl formate is occasionally used, especially when it is desired to obtain a film of high strength by using a cellulose

nitrate of high viscosity. It gives solutions of lower viscosity than either butyl or amyl acetate, but is not so efficient in preventing water blush. It also possesses the property of being a solvent for some types of cellulose acetate. It is a solvent for ester gum, copal ester, cumarone, benzyl abietate and mastic ; it partly dissolves shellac, and in the presence of alcohol will dissolve glyceryl phthalate resins. It is miscible with castor, linseed and other oils and with hydro-carbons, but not with water to any considerable extent. It will not dissolve hard copals.

The B.E.S.A. Specification, D21,[3] is as follows : S.G. ·885. B.R. 96°–110° C. Esters 85% min. Acidity 0·02% max. Pure butyl formate has S.G. 0·9108. B.P. 106°–107°. V.P. 23. L.H. 87. S.H. ·46. R.I. 1·389. Vis. ·59. It forms constant-boiling mixtures, with 16·5% of water boiling at 83·8° ; with 23·7% of butyl alcohol boiling at 105·8° ; and a ternary mixture consisting of 68·7% of ester ; 10% of butyl alcohol ; and 21·3% of water boiling at 83·6°.

Amyl Formate. $H.COO.C_5H_{11}$

Amyl formate is sometimes preferred to amyl acetate, especially for use in the manufacture of leather-cloth, as its odour is less pronounced and is suggestive of leather. Its volatility is very similar to that of *n*-butyl acetate, for which it can be substituted as required.

The B.E.S.A. Specification, D20,[3] is as follows : B.R. 110°–130°. S.G. ·880–·885. F.P. about 80° F. (26° C.). Acidity 0·05% max. Anhydrous, colourless. The technical ester is a mixture of the formates of isomeric and homologous alcohols, but consists mainly of isoamyl formate. Vis. ·8.

Amyl formate is a good solvent for cellulose nitrate, colophony, ester gum, copal ester, benzyl abietate, cumarone, mastic ; it is miscible with castor and linseed oils and with hydrocarbons, but not with water. It dissolves 0·3% of water at 20° C. It does not dissolve cellulose acetate or hard copals ; it partly dissolves shellac and will dissolve glyceryl phthalate resin in the presence of an alcohol. Solutions of cellulose nitrate in amyl formate are slightly less viscous than those of corresponding concentration in *n*-butyl acetate.

The following binary constant-boiling mixtures are known :—

Isoamyl formate 79%.	Water 21%.	B.P. 90·2° C.
n-Amyl formate 71·6%.	Water 28·4%.	,, 91·6° C.
Isoamyl formate 74%.	Isoamyl alcohol 26%.	,, 123·6° C.
n-Amyl formate 57%.	*n*-Amyl alcohol 43%.	,, 130·4° C.

Ethyl Propionate. $CH_3 . CH_2 . COO . CH_2 . CH_3$

An ester having a strong odour reminding of pineapples. It is available technically,[9] but is not widely used, as it offers no marked advantage over other esters of its class.

Characteristics : S.G. ·88. B.P. 92°–99°. F.P. 15° C. (60° F.). Vis. ·55.

It is a solvent for cellulose nitrate, colophony and ester gum, but not for cellulose acetate.

***n*-Butyl Propionate.** $CH_3 . CH_2 . COO . CH_2 . CH_2 . CH_2 . CH_3$

This ester can be used in the place of amyl acetate when a solvent of somewhat lower volatility is required, as in the case of a lacquer to be applied under excessively humid conditions. Its odour, reminding of apples, is less objectionable to most persons than is that of amyl acetate. It is non-toxic.

Butyl propionate is manufactured in the United States from the residue arising from the manufacture of acetone by the fermentation of seaweed. This residue consists largely of calcium propionate together with small quantities of the acetate and butyrate.[10]

Butyl propionate is a good solvent for cellulose nitrate, ester gum, copal ester, benzyl abietate, mastic, dammar, cumarone, elemi ; but does not dissolve cellulose acetate, hard copals, sandarac, zanzibar or glyceryl phthalates. It partly dissolves shellac. It is miscible with castor, linseed and other oils and with hydrocarbons, but not with water. It dissolves water to the extent of 0·452% at 7°, 0·513% at 16°, 0·576% at 22·5°, and 0·691% at 30°.

Technical butyl propionate has the following characteristics : S.G. ·878–·883. B.R. 135°–155°. Esters 95% min. Acidity ·05% max. Dil. rat. toluene 2·0, petroleum 1·1.

*A.S.T.M. Butyl Propionate D*320–40[4] has S.G. ·872–·878 at 20°. Esters 90–93%. Acidity ·02% max. B.R. up to 115°, none ; 130°, 20% max. ; 138°, 60% max. ; above 168°, none. Residue ·005% max.

Characteristics of the pure ester : S.G. ·883. R.I. at 25° 1·3982. B.P. 146°. F.P. 45° C. (113° F.).

Amyl Propionate

Amyl propionate is of value for brushing lacquers where a rather slower rate of evaporation is required than is given by amyl acetate. Like the latter, its composition varies considerably. The following figures show the characteristics of a high-grade lacquer quality: S.G. ·870–·873. B.R. 140°–170°. F.P. 105° F. (40° C.). Esters 85–100%. Acidity 0·02% max. as propionic acid. Dil. rat. toluene 1·6, petroleum 0·9. Pure iso-amyl propionate has: B.P. 160°. L.H. 63. S. H. ·46. R.I. 1·406. F.P. 63° C. Vis. ·93. Dielec. const. 4·25. Its odour is less objectionable than that of amyl acetate, being milder and more like apples. It is non-toxic. It has much the same solvent properties as amyl acetate, but is somewhat slower in its action, and gives slightly more viscous solutions. It is a solvent for cellulose nitrate, ester gum, benzyl abietate, copal ester, cumarone, elemi, mastic, sandarac, kauri and soft copals, but not for cellulose acetate, shellac, dammar or hard copals. It is miscible with castor and linseed oils and with hydrocarbons, but is not miscible with water.

Ethyl Butyrate. $CH_3 . CH_2 . CH_2 . COO . C_2H_5$

This substance is a solvent intermediate between ethyl and *n*-butyl acetates in solvent properties. It is a rapid solvent for cellulose nitrate, and yields solutions having viscosities somewhat lower than those of *n*-butyl acetate. Ethyl butyrate is a non-toxic substance having a powerful "pineapple" odour, and is widely used for flavouring purposes.

Characteristics of Pure Ester: B.P. 120°. S.G. ·88. F.P. 23° C. Vis. ·67.

It is a solvent for ester gum, colophony, cumarone, manila, mastic, gutta percha resin and ethyl cellulose, but not for cellulose acetate or glyceryl phthalate resin.

n-Butyl Butyrate. $CH_3 . CH_2 . CH_2 . COO . C_4H_9$

In recent years this ester has been used as a cellulose nitrate solvent to a small extent. It consists usually of a mixture of the *n*-butyl esters of *n*- and iso-butyric acids, the former preponderating. S.G. ·870–·880. B.R. 160°–165° R.I. about 1·405. F.P. 51° C. (124° F.). Vis. ·97 at 25°.

It is a solvent for cellulose nitrate, ester gum, mastic, cumarone, dammar, elemi, shellac, zinc resinate; but not for

cellulose acetate, sandarac, zanzibar, hard copals. *n*-Butyl butyrate dissolves water to the extent of 0·380% at 10°; 0·424% at 16°; 0·497% at 25°; an 0·574% at 33°. Its odour is strong and reminiscent of apples; it is non-toxic.

n-Butyl butyrate is useful when it is desired to have a solvent that evaporates somewhat more slowly than amyl acetate. It imparts good brushing flow and gloss to lacquers.

Benzyl Formate. $C_6H_5 . CH_2 . OOC . H$

Benzyl formate is similar in character to benzyl acetate, but is of somewhat greater volatility. Its odour is less pronounced and is suggestive of leather. It is made by the direct esterification of benzyl alcohol with formic acid. It is not widely used.

Physical Characteristics: S.G. 1·08–1·09. R.I. 1·519–1·520. B.R. 200°–202°.

It is a good solvent for cellulose acetate and nitrate, for ester gum, copal ester, benzyl abietate, cumarone, glyceryl phthalate resins, and is miscible with castor and linseed oils, and with aromatic and petroleum hydrocarbons.

Benzyl Acetate. $C_6H_5 . CH_2 . OOC . CH_3$

Prepared by the direct esterification of benzyl alcohol with acetic acid or by the action of anhydrous sodium acetate on benzyl chloride. It is an excellent solvent of medium volatility for cellulose nitrate and for some forms of cellulose acetate. Its odour is powerful but pleasant, and is suggestive of jasmine flowers.

Physical Characteristics: S.G. 1·060–1·062. R.I. 1·502–1·503. B.R. 215°–216°. F.P. 102° C. (216° F.). Esters 99–100%. Non-toxic, Impurities: traces of benzyl alcohol, chlorotoluene, dibenzyl ether and dibenzyl.

It yields solutions, of moderate viscosity, of cellulose acetate and nitrate, and has a temporary softening effect on films made of these materials. It imparts good brushing flow and high gloss. It is a good solvent for ester gum, copal ester, benzyl abietate, cumarone, mastic, castor and linseed oils, and in conjunction with alcohols it dissolves glyceryl phthalate resins and shellac; it will dissolve copals on prolonged heating. It is miscible with aromatic and petroleum hydrocarbons.

Ethyl Lactate. $CH_3 . CH(OH) . COO . C_2H_5$

This is one of the most important of the high-boiling solvents for both cellulose nitrate and acetate; it has exceptionally high solvent powers, tolerating considerable dilution with non-solvents. It suffers from two defects: the composition of the technical ester varies rather widely, and its rate of evaporation is slower than is desirable. This slowness is of advantage where brushing lacquers are concerned, or where the lacquer has to be applied in a cold, humid atmosphere; it also favours the production of films with a high gloss, but films produced by means of this vehicle have a tendency to remain soft for a considerable time beyond what might be considered to be a normal drying period. It imparts good flowing properties to lacquers, allowing them to be applied in thin coats over widely varying types of surface with the production of smooth, impermeable, and uniform films.[7]

Compared with amyl and butyl acetates, its solvent action on cellulose nitrate is distinctly slower and its solutions are of decidedly higher viscosity, but they will tolerate two to three times as much non-solvent diluent; quantities of water—up to 25%—can be added without causing precipitation or blushing on subsequent evaporation. The dilution latitude of solutions of cellulose acetate in ethyl lactate is two to twelve times as great as those of other solvents.

Ethyl lactate is manufactured by the esterification of lactic acid obtained from the fermentation of sugar solutions with *Bacillus acidi lactici*. It has also been made by a purely synthetical method [11] as follows: Acetaldehyde is first obtained, either by the hydration of acetylene or by the dehydrogenation of alcohol, and is combined with hydrocyanic acid to form lactonitrile (acetaldehyde cyanhydrine). This nitrile is converted directly into ethyl lactate by treatment with alcohol and hydrochloric or sulphuric acid, ammonium chloride or sulphate being formed simultaneously. The ammonium salt is separated by mechanical means, and the ester is purified by fractional vacuum distillation; yields of 90% are said to be obtained.

Ethyl lactate may contain lactides or inner esters of lactic acid; these are solvents with higher boiling-points than ethyl lactate, and cause a widening of the boiling-range and of the limits for the other physical properties.

British Standard Ethyl Lactate No. 663—1936 [3] has: S.G.

1·032–1·040 (1·026–1·034 at 20°). B.R. 135–160, 95% min. Residue ·01% max. Esters 95% min. Acidity ·025% max. Clearly miscible with water and with petroleum ether in all proportions.

*A.S.T.M. Ethyl Lactate D*321–40 [4] has S.G. 1·020–1·036 at 20°. Esters 96–100%. Acidity ·08% max. as lactic acid; B.R. up to 102°, none, 139° 10% max., 155°, 90% min., above 173°, none. Residue ·005% max. Clearly miscible with gasoline in all proportions. Pure ethyl lactate has B.P. 154·5°. R.I. 1·4118. F.P. 46° C. (115° F.). V.P. 1·8. Cub. exp. ·00098.

Ethyl lactate, when pure, is nearly odourless; technical products have a weak odour resembling that of ethyl butyrate, and should not leave a disagreeable odour on evaporation.

Ethyl lactate is a solvent for both cellulose acetate and nitrate, also for benzyl and ethyl cellulose, colophony, manila, kauri, pontianac, shellac, benzyl abietate, thio-urea, cyclohexanone-formaldehyde resins, glyceryl phthalate resins, vinyl acetate resins, basic dyes; and is miscible with raw linseed oil, blown castor oil, aromatic hydrocarbons, low-boiling hydrocarbons, white spirit and water. It will dissolve hard copals on prolonged boiling. It will not dissolve rubber chloride.

Iso-propyl Lactate. $CH_3 . CH(OH) . COO . CH(CH_3)_2$

This ester, like ethyl lactate, is a solvent for both cellulose acetate and nitrate; it is better solvent for ester gum than is ethyl lactate. It also dissolves colophony, shellac, benzyl abietate, cumarone, glyceryl phthalate and vinyl acetate resins. Technical preparations have S.G. ·994–·998. B.R. 155°–165° (95%). Esters 95% min. Acidity ·05% max. as lactic acid.

Pure material has S.G. at 20° ·998. R.I. at 25° 1·408. B.P. 166–8°.

Butyl Lactate. $CH_3 . CH(OH) . COO . C_4H_9$

n-Butyl lactate is made by the direct esterification of lactic acid with butyl alcohol. Like other esters of lactic acid, it exists in two stereoisomeric modifications. When pure, it is a colourless liquid, but the technical article is often slightly brown. It is practically devoid of odour, and is non-toxic.

Physical Characteristics : S.G. ·984–·988. B.R. 185°–195°. Esters 95% min. Acidity 0·05% max.

Pure material has S.G. at 20° ·973. R.I. 1·422. B.P. 185°. L.H. 77. M.P. –43° C. F.P. 160° F. (71° C.).

Water dissolves 3·4% at 25° C. Butyl lactate dissolves 13% of water at 25° C., but it is not hygroscopic.

The commercial product varies rather widely in quality, owing to the presence of condensation products such as lactide.

It is a good solvent for ester gum, and renders this resin compatible to some extent with cellulose acetate ; it readily dissolves cellulose nitrate, glyceryl phthalate resin, cumarone ; it has a moderate solvent action on cellulose acetate, rubber chloride, copal ester, benzyl abietate, shellac, mastic. It is miscible with castor and linseed oils, and with aromatic and petroleum hydrocarbons, but not with water. It has a high tolerance for diluents.

It imparts brilliance and tenacity to films, but tends to cause softness for a considerable period owing to its slow rate of evaporation.

Butyl lactate tends to prevent the formation of a skin on oil varnishes and paints.

Iso-butyl Lactate. $CH_3 . CH(OH) . COO . CH_2 . CH\begin{<}CH_3\\CH_3\end{>}$

Iso-butyl lactate is similar to *n*-butyl lactate in solvent properties, but it evaporates somewhat more rapidly. This ester is available technically, and has B.R. 168°–200° C. S.G. ·974–·978. Acidity ·05% max. as lactic acid. Esters 95% min. Pure material has S.G. at 20° ·97. R.I. at 25° 1·418.

sec-Butyl Lactate. $CH_3 . CH(OH) . COO . CH\begin{<}CH_2 . CH_3\\CH_3\end{>}$

Secondary butyl lactate [12] is an ester of similar character to the other isomers and has S.G. ·974 at 20°. B.P. 180°. It has a faint fruity odour, and is but slightly soluble in water.

Amyl Lactate. $CH_3 . CH(OH) . COO . C_5H_{11}$

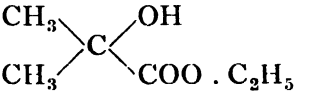
This ester is used as a softener or as a high-boiling solvent when it is desirable to prolong the period of drying of a cellulose-nitrate lacquer. It is not widely employed.

Physical Characteristics : S.G. ·968–·972. B.P. about 210°. R.I. at 25° 1·424. Acidity 0·05 % max. Like other esters of lactic acid, the technical product is apt to vary considerably in composition, and to contain lactides.

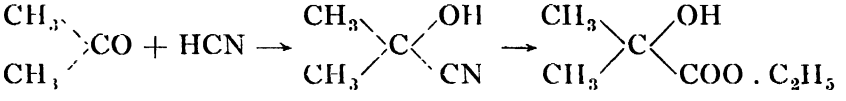
It is a solvent for cellulose nitrate, ester gum, copal ester, benzyl abietate, shellac, cumarone and mastic. It does not dissolve cellulose acetate, nor hard copals, although the latter can usually be dissolved on prolonged boiling. It dissolves glyceryl phthalate resins in conjunction with an alcohol. It is miscible with castor and linseed oils and with hydrocarbons, but not with water.

Its odour is weak, somewhat like that of brandy; it is non-toxic.

Ethyl Hydroxy-iso-Butyrate.



Ethyl hydroxy-iso-butyrate, known in the trade as ethyl oxybutyrate,[13] is a synthetic ester made by condensing acetone with hydrocyanic acid to form acetone cyanhydrine, which is then simultaneously hydrolysed and esterified by treatment with ethyl alcohol and hydrochloric acid [14] :



It is a colourless liquid, having a mild, pleasing odour ; it is highly resistant to hydrolysis, and is preferred to ethyl lactate, being more homogeneous and of somewhat higher volatility.

Physical Characteristics : S.G. at 20° ·978–·986. B.R. 142°-146°. Esters, 96–100%. It dissolves both cellulose acetate and nitrate, but its action is rather slow ; solutions of the nitrate in it are about twice as viscous as those of corresponding concentration in ethyl lactate, but less viscous than those in amyl acetate. Its tolerance to dilution with hydrocarbons is much the same as that of ethyl lactate for cellulose nitrate solutions, but not so high for the acetate.

Its rate of evaporation is low, and it tends to leave films, which remain soft for a considerable period, but it imparts a high gloss to films, and has a good brushing flow.

Methyl oxybutyrate is also manufactured. It has S.G. ·987 at 20°. R.I. 1·408. B.P. 150°.

Butyl Glycollate. $HO . CH_2 . COO . C_4H_9$

This is a lower-boiling variant of butyl lactate, having good solvent powers for many resins and cellulose nitrate. It does not dissolve cellulose acetate. It is a solvent for colophany, ester gum, manila, elemi, shellac, mastic, vinyls, glyptals and sandarac. S.G. 1·013 at 20°. B.R. 178°–186°. F.P. 155° F. (68° C.). Dil. rat. benzene 7·6. E.R. 148.

Ethyl Acetyl Glycollate. $CH_3 . COO . CH_2 . COO . C_2H_5$

This is a high-boiling solvent for cellulose acetate and nitrate. It has the following characteristics: S.G. at 20° 1·094. B.R. 181°–195°. Esters 98–100%. F.P. 180° F. (82° C.).

It is a colourless liquid, having a faint ester-like odour.

Ethyl Benzoate. $C_6H_5 . COO : C_2H_5$

This is a solvent of the " high-boiling " class, and suffers from the defects inherent in this class. It is useful for imparting good brushing properties to cellulose lacquers, and gives films of high gloss, but these films tend to remain soft for an unduly long period ; it can even be used as a plasticiser.

Characteristics : S.G. 1·051–1·053. B.R. 212°–215°. R.I 1·505–1·506. Esters, 98–100%. M.P. — 34°. Vis. 2·2. Elec. cond. $< 1 \times 10^{-9}$. Dielec. const. 6. Cub. exp. ·00092.

The technical article is usually one of high purity. Ethyl benzoate is a solvent for cellulose acetate and nitrate, ethyl cellulose, ester gum, sandarac, mastic, shellac, cumarone, glyceryl phthalate resin, benzyl abietate, but not for hard copals, except on prolonged boiling. It is miscible with castor and linseed oils and with hydrocarbons, but not with water.

Its odour is powerful but pleasant ; it is non-toxic and is stable to light.

Methyl Benzoate

Methyl benzoate, known also as " Oil of Niobe," has a somewhat less pronounced odour than the ethyl ester.

Characteristics : S.G. 1·093–1·094. B.R. 198°–200°. R.I. 1·515–1·517. B.P. 198·1°. Elec. cond. $1·37 \times 10^{-3}$. Diel. const. 6·58. Vis. 2·07.

It is a solvent for cellulose acetate and nitrate, ester gum, cumarone, rubber. It is miscible with oil, but not with water. Non-toxic.

Di-ethyl Carbonate. $(C_2H_5O)_2 . CO$

This is a colourless liquid, having a weak odour resembling that of ethyl butyrate, with a curious faintly lachrymatory after-effect similar to that of ethyl chloro-acetate.

It is manufactured by treating phosgene (carbonyl chloride) with alcohol,[15] either by refluxing them together and extracting the ester with a suitable solvent, such as carbon tetrachloride, or by treating alcohol in excess with phosgene vapour,[12] and in other similar ways. Phosgene is produced from producer gas and chlorine by passing them over activated carbon at 125°–150° C.

Diethyl carbonate is also produced when ethyl chloro-formate and alcohol are treated with di-methyl aniline.

Physical Characteristics : S.G. ·976–·980. R.I. 1·385. B.P. 127°. .R. 120°–130°. V.P. about 30 at 20°. F.P. 30° C. (86° F.). L.H. 73. S.H. ·46. E.R. 14. Elec. cond. 17×10^{-9}. Dielec. const. 3·15.

Di-ethyl carbonate is miscible with castor oil, aromatic hydrocarbons, and most organic solvents, but non-miscible with some petroleum hydrocarbons. It dissolves 2·6% of water at 20° C. It is not, by itself, a good solvent for cellulose acetate or nitrate, but the addition of an alcohol or an ester greatly increases its solvent power for the latter, and also renders it a solvent for benzyl cellulose.

Its solutions of cellulose nitrate are more viscous than solutions of corresponding concentration in butyl acetate, and these solutions have but a poor tolerance for hydrocarbons ; the presence of a small proportion of ethyl lactate considerably increases the tolerance.

Di-ethyl carbonate is a solvent for ester gum, cumarone, mastic, colophony and thus ; the presence of 5 to 10% of anhydrous alcohol renders it a solvent for elemi, sandarac, manila, kauri. Non-solvent for copal, congo, copal ester, glyceryl phthalate resin, benzyl resin.

References

[1] U.S. Pat. 1467091 ; 1467105.
[2] Brit. Pat. 131088.
[3] British Standards Institution, 28 Victoria Street, S.W.1.
[4] American Society for Testing Materials, 260 S. Broad Street, Philadelphia.
[5] *Cf.* W. S. SIMMONS. " Alcohol," Macmillan & Co. Ltd.
[6] The Sharples Solvents Corporation, Philadelphia, U.S.A.

[7] Asiatic Petroleum Co. Ltd., London.
[8] PARK and HOPKINS. *Ind. Eng. Chem.*, 1930, p. 826.
[9] Holzverkohlungs Industrie, Konstanz.
[10] *Cf.* B.P. 396968.
[11] Canadian Electro-Products Company, Shawinigan ; American Cyanamide Co., N.Y., U.S.A. ; Brit. Pat. 257907.
[12] *Cf.* U.S. Pat. 1956972.
[13] American Cyanamide Company, N.Y., U.S.A.
[14] *Cf.* U.S. Pat. 1926510 ; 1926511.
[15] U.S. Pat. 1603703 ; 1638014 ; 1603689.

CHAPTER V

GLYCOLS AND THEIR ETHERS

Ethylene Glycol. $HO . CH_2 . CH_2 . OH$

ETHYLENE glycol, or more simply glycol, is a liquid with properties intermediate between those of ethyl alcohol and glycerin. It is colourless and odourless, has a bitter-sweet taste, somewhat viscous, very hygroscopic, and miscible in all proportions with water, acetone, alcohol, butanol and furfural, non-miscible with hydrocarbons, ether, carbon tetrachloride, carbon disulphide or chloroform. B.R. 190°–200°. B.P. (pure) 197·2°. S.G. 1·115–1·118. F.P. 240° F. (115° C.). M.P. about −14°. S.H. ·575. R.I. 1·43. L.H. ·194. Vis. 17 at 25°. S. ten. at 25° 53.

The crystallising points of mixtures of glycol and water are as follows :—

Per cent. Glycol.	S G	°F	°C.
25	1·038	+ 10	−12
30	1·045	+3	−16
35	1·052	−5	−20
40	1·058	−15	−26
45	1·064	−26	−32

It is a solvent for some dyes, and gelatinises cellulose nitrate, but it is not a solvent which finds application in the preparation of lacquers or varnishes. The method by which it is manufactured is described under ethylene glycol mono-ethyl ether.

The toxicity of glycol is in question, when taken internally it appears to form the poisonous substance oxalic acid.

Ethylene Glycol Mono-Acetate
$CH_3 . COO . CH_2 . CH_2 . OH$

This is an odourless, colourless liquid, miscible with water and with aromatic hydrocarbons, but non-miscible with paraffins or linseed oil. B.R. 185°–195°. S.G. 1·11. F.P. 215° F. (102° C.). It is a high-boiling solvent for cellulose nitrate and acetate, elemi and colophony. It partly dissolves

mastic, but not shellac, kauri, sandarac, dammar, zanzibar, hard copals, ester gum, and cumarone.

Ethylene Glycol Di-Acetate

$CH_3 . COO . CH_2 . CH_2 . OOC . CH_3$

The diacetate sometimes called ethylene diacetate is made by heating ethylene dichloride with potassium or sodium acetate in the presence of about 5% of glycol, which acts as a flux,[1] under a pressure of 125–150 lb. per square inch.

It is a colourless liquid having a slight odour, reminding of ethyl acetate. S.G. 1·15. B.R. 186°–190°. Esters 98% min. B.P. 190. R.I. 1·415. F.P. 220° F. (105° C.).

It is a solvent for cellulose acetate and nitrate, mastic, colophony, and gum camphor, but not for shellac, kauri, sandarac, dammar, zanzibar, hard copal, ester gum, cumarone. It is not miscible with petroleum or linseed oil, and its solutions have a low tolerance for toluene. It dissolves 21% of water at 20° C.

Ethylene Glycol Mono-methyl Ether

$CH_3O . CH_2 . CH_2 . OH$

Known also as methyl glycol, methoxy ethanol and methyl cellosolve,[2] it is the only ether of this group which is a solvent for low viscosity cellulose acetate as well as for the nitrate. It also dissolves shellac, kauri, mastic, sandarac, elemi and colophony, and to some extent ester gum, zanzibar and dammar. It is miscible with aromatic and light paraffin hydrocarbons, and also with water, but not with heavy paraffins or linseed oil. It is a colourless liquid of mild odour, and is a solvent for spirit-soluble dyes. S.G. ·968–·975. B.R. 124°–125°. F.P. 107° F. (42° C.). Auto-ignition temp. 288° C. R.I. at 25°, about 1·402. Vis. 1·7. It forms a constant-boiling mixture with water containing 24·7% of the ether and boiling at 100° C. It is practically odourless; under certain conditions it decomposes rapidly into acetaldehyde and methanol.

Methyl cellosolve forms mixtures with water having specific gravities over 1 at 15° C. in the range of 20–80% of water with a maximum of 1·014 at 60%.

The acetic ester, *ethylene glycol mono-methyl ether monoacetate*, is a colourless liquid having a pleasant, weak odour. It is a solvent for both cellulose acetate and nitrate and for vinyl acetate. It is miscible with water in all proportions.

S.G. 1·008–1·011 at 20°. B.R. 138°–152°. B.P. 144°. F.P. 44° C. (111° F.).

Ethylene Glycol Mono-ethyl Ether
$C_2H_5O \cdot CH_2 \cdot CH_2 \cdot OH$

The mono-ethyl ether, known also as ethyl glycol ethoxy ethanol and " cellosolve," [2] is the most important solvent of this class. It is a colourless, nearly odourless, stable liquid, and is a good solvent for cellulose nitrate. It has the curious property of developing a haze when clear solutions of certain resins are mixed with clear solutions of cellulose nitrate. Ordinary ester gum, although soluble in the ether, is not compatible with a solution of cellulose nitrate, but an addition of alcohol-soluble dewaxed dammar ensures compatibility, provided that the proportion of ester gum is not more than three times that of the dammar. Small additions of glyceryl phthalate resin also render ester gum compatible. The addition of other solvents will often remove the haze, benzyl alcohol, amyl acetate and ethyl lactate being suitable for this purpose. In the absence of resins, solutions of cellulose nitrate in ethylene glycol mon-ethyl ether have a high tolerance for dilution with non-solvents ; thus for toluene it varies from 5·6 to 6·6, for butyl alcohol it is about 7·5, and for gasoline 1·2 to 1·5, depending on the particular quality of the cellulose nitrate, and is therefore similar to ethyl lactate in this respect.

It has been recorded [3] that, like acetone and ethyl acetate, the methyl and ethyl ethers of ethylene glycol sometimes yield opaque films of cellulose nitrate, especially when the drying operation is conducted in a highly humid atmosphere. This may be partly due to the fact that these ethers are powerful solvents for water (*cf.* p. 38). Notwithstanding these defects, the ethers offer the advantage over most other solvents of similar boiling-point in having but a slight odour. They are definitely narcotic, but probably not dangerously so.

Ethylene glycol mono-ethyl ether can be manufactured by several methods, the first step in the process being the preparation of ethylene chlorhydrine (*q.v.*). From this point the process may proceed by several routes ; thus one. method is to transform the chlorhydrine to ethylene glycol [4] by passing the constant-boiling mixture, resulting from the distillation of the ethylene chlorhydrine solution in water, in vapour

form up a tower, down which sodium carbonate solution is falling; hydrolysis takes place and the glycol, dissolved in the solution of salt, which is simultaneously formed, passes to the bottom of the tower; carbon dioxide, acetaldehyde, steam and other volatile substances passing away from the top. The ethylene glycol is subsequently recovered from the salt solution by fractional distillation. The ethyl ether of the glycol can be made by refluxing for three hours a mixture of two molecular proportions of the glycol with two of sodium hydroxide and one of diethyl sulphate, and then fractionally distilling the mixture under diminished pressure; a yield of about 60% being obtained.[5] The ether is also made from ethylene chlorhydrine by first converting this into ethylene oxide and adding this, while stirring, to cold ethyl alcohol, containing 1% of sulphuric acid, the product being neutralised and fractionally distilled. Other ethers of ethylene glycol may be made in a similar manner by the use of other alcohols or phenols, such as methyl, propyl, or butyl alcohol; yields of 90% being obtained.[6] Catalysts other than sulphuric acid may also be used.[7] The conversion of ethylene chlorhydrine into the ethylene oxide required for the above process can be effected by passing the chlorhydrine at high temperatures over solid bases or through suspensions of lime or soda-lime in water [8]; solutions as dilute as 8% of ethylene chlorhydrine can be used for this process, and strong alkalis may also be employed.

The present trend is to produce ethylene oxide, without the use of chlorine, by directly combining ethylene and oxygen by treatment under high pressure and temperature with silver catalysts.[9]

*The A.S.T.M. Specification D*331–35 requires S.G. at 20°, ·927–·933. B.R., up to 128°, none; 128–132, 5% max.; below 136°, 95% min.; above 137°, none. Non-volatile matter, ·005%. Acidity, ·02% acetic. Clearly miscible with gasoline.

D.T.D. 395—1940 [18] requires S.G. ·934–·938. F.P. 40° C. min. R.I. 1·4063–1·4079. *p*H 5·8–7·0. B.R., 125° min., 130–136° 95% min. No turbidity with water.

The pure material has B.P. 134·5°. R.I. 1·408. Vis. 2·1. V.P. at 20° 4·5 mm. F.P. 40·° C. (104° F.). Auto-ignition temp. 238° C. It is miscible with water in all proportions, also with hydrocarbons. It is a solvent for cellulose nitrate, but

not for the acetate except on heating ; it dissolves ester gum, dewaxed dammar, glyceryl phthalate resin, benzyl abietate, vinyl acetate and cyclohexanone-formaldehyde resin. It partly dissolves shellac, mastic, and cumarone, and will dissolve hard copals on prolonged heating. It will not dissolve copal ester or rubber chloride. Exposure to sunlight tends to cause decomposition.

Ethylene Glycol Diethyl Ether

$C_2H_5O \cdot CH_2 \cdot CH_2 \cdot OC_2H_5$

Ethylene glycol diethyl ether is a colourless liquid having a faint odour. B.P. 121°. S.G. ·853. R.I. 1·3914. It is a solvent for cellulose nitrate, but not for the acetate. It also dissolves ester gum, elemi, zanzibar, cumarone, dammar, mastic, kauri, shellac, but not hard copal or sandarac. It is moderately soluble in water.

Ethylene Glycol Mono-ethyl Ether Mono-acetate

$C_2H_5O \cdot CH_2 \cdot CH_2 \cdot OOC \cdot CH_3$

This is a colourless liquid with a weak, pleasant, ester-like odour, known commercially as " Cellosolve Acetate." [2] It is a solvent for cellulose nitrate, giving viscous solutions, and its dilution ratios for solutions of this under standard conditions are for toluene 3·0, gasoline 1·5, turpentine 2·8.

*The A.S.T.M. Specification D.*343–35 [10] requires S.G. ·968–·976 at 20°. B.R. up to 145°, none ; 150°–160°, 90% min. ; above 165° none. Esters 95%–96%. Acidity ·024%. Residue ·03% max. Clearly miscible with 19 vols. gasoline. The material also has B.P. 156°. S. ten. 31·8. Vis. 1·2. S.H. ·494. V.P. 2. Elec. cond. 2×10^{-8}. F.P. 124° F. (51° C.). R.I. at 25° about 1·405. Water dissolves 22% at 20°.

It is a solvent for cellulose nitrate, ester gum, polystyrene, cumarone, mastic, kauri, shellac, gutta percha resin, rubber chloride. It partly dissolves elemi and sandarac, but not cellulose acetate, zanzibar, or hard copal.

Ethylene Glycol Mono-*n*-Butyl Ether

$C_4H_9O \cdot CH_2 \cdot CH_2 \cdot OH$

The mono-butyl ether is a high-boiling solvent known also as butyl glycol, and commercially as " Butylcellosolve." [2] It is a good solvent for cellulose nitrate, but rather slow in its

action. Its dilution ratio under the standard condition is 3·5 for toluene, 2·3 for gasoline, and 0·375 for water.

It is a solvent for shellac, sandarac, mastic, kauri, gutta percha resin, cumarone, ester gum, and elemi. It is miscible with water, linseed oil and with hydrocarbons. It partly dissolves dammar and zanzibar, but not copal or cellulose acetate.

*A.S.T.M. Specification D.*330–35 [10] requires S.G. ·899–·905 at 20°. B.R. up to 163° none; 167°, 5% max.; 171° 95% min., above 174° none. Residue ·005% max. Clearly miscible with 19 vols. gasoline. Acidity ·02% acetic max.

It is a colourless liquid of mild odour. R.I. about 1·4177. B.P. 171°. F.P. 140° F. (60° C.). Auto-ignition temp. 244° C. Vis. 3·3.

It is recommended for brushing lacquers and for applying second coats over existing coats of cellulose nitrate, also for reducing the viscosity of lacquers.

Propylene Glycol. $CH_3 . CH(OH) . CH_2 . OH$

This glycol, 1·2 propandiol, is available commercially in small quantities, it is a colourless, somewhat viscous, bitter tasting, non-poisonous liquid, hygroscopic and soluble in water. It has S.G. 20° 1·035. Vis. 45. B.P. 188°. R.I. 1·432 at 25°. F.P. 210° F. (99° C.). Its solvent properties are similar to those of ethylene glycol. The diacetate has B.R. 182–184°.

Butylene Glycol. $CH_3 . CH(OH) . CH_2 . CH_2 . OH$

1·3 Butylene glycol is prepared by hydrogenating aldol.[17] It is a syrupy, colourless, odourless liquid similar in character to ethylene glycol.

It has B.R. 204°–208°. B.P. (pure) 207°. S.G. 1·01–1·03. R.I. 1·442. F.P. 104° F. (40° C.). It is soluble in water, alcohols, ethyl acetate, acetone, but not in castor oil, hydrocarbons or ether. It is a solvent for shellac and colophony, and partly for dammar and cumarone; it does not dissolve cellulose esters or ethers or ester gum, vinyl resin and rubber chloride, it plasticises rubber latax.

The *mono-ethyl ether* has B.P. 164°. S.G. ·886. R.I. 1·4162.

Butylene Glycol Diacetate

Butylene glycol diacetate is a powerful solvent for both cellulose esters and ethers, also for colophony, ester gum,

alkyld resins, cumarone, vinyl acetate. It partly dissolves shellac, mastic, congo manila and rubber chloride, but not dammar, sandarac or vulcanised rubber.

It is a colourless, nearly odourless, bitter-tasting liquid, having S.G. 1·026–1·034. B.R. 204–210 (90%). B.P. 208°. R.I. 1·42. Dil. rat. toluene 2·3. It is stable to light and non-toxic. Water dissolves 4·8% at 20°.

Diethylene Glycol. $HO . CH_2 . CH_2 . O . CH_2 . CH_2 . OH$

Diethylene glycol, or, as it is more correctly named, sym. di-hydroxy-di-ethyl ether, is produced by the partial dehydration of glycol, also, and more readily, by the combination of ethylene oxide and glycol; the former is produced by passing ethylene chlorhydrine over solid bases or through suspensions of lime or soda lime at elevated temperatures.[11] Tri-ethylene and tetra-ethylene glycols are obtained as by-products.

Physical Characteristics : Di-ethylene glycol is a colourless, almost odourless liquid, considerably more viscous and more hygroscopic than ethylene glycol. Rinkenbach [12] gives the following figures for the comparative viscosity of the mono- and di-ethylene glycols :

Temperature.	Diethylene Glycol.	Ethylene Glycol.
°C.	Poises.	Poises.
15	0·50	0·26
17·5	0·44	0·23
20·0	0·38	0·21
22·5	0·33	0·19
25·0	0·30	0·17
27·0	0·27	0·16

S.G. 1·121. S.P. —10·5°. F.P. 124° C. (255° F.). R.I. 1·4475; L.H. 140; I.P. about 130°. Auto-ignition temp. 229° C. B.P. 244·5. Miscible with water, alcohols, glycols, acetone, furfural, glycol diacetate, chloroform, esters.

Diethylene glycol is non-miscible with ether, benzene, toluene, carbon tetrachloride, linseed oil, castor oil, petroleums. It dissolves cellulose nitrate, dyes, but is a non-

solvent for ester gum, shellac, cumarone, copals, cellulose acetate ; mastic is partly soluble.

Diethylene glycol mono-acetate is a solvent for cellulose acetate and nitrate, colophony, and gum camphor. It partly dissolves cumarone, mastic, elemi, and kauri, but not ester gum, shellac, copals, sandarac. It is miscible with water and aromatic hydrocarbons, but not with linseed oil or petroleum.

Diethylene Glycol Mono-Ethyl Ether

$C_2H_5O . CH_2 . CH_2 . O . CH_2 . CH_2 . OH$

The above name commonly given to this ether is incorrect ; a more correct name is hydroxy-ethoxy-ethyl ether. Commercially, it is known as "Carbitol." [2] It is made [13] by the action of ethylene oxide on the sodium compound of ethylene glycol mono-ethyl ether (*q.v.*). It is a good solvent for cellulose nitrate, shellac, kauri, mastic, sandarac, copal, elemi, cumarone, colophony, and dyes. It partly dissolves ester gum, zanzibar and dammar, but does not dissolve cellulose acetate or castor oil. S.G. ·9996 at 15°. B.R. 180°–200°. B.P. 198°. Miscible with water in all proportions, but not with mineral spirit. Hygroscopic. R.I. about 1·43. F.P. 200° F.

It is used in the manufacture of textile soaps and in dye printing.

The mono-acetate is softener-solvent for cellulose nitrate and acetate. It has B.P. 198°.

It dissolves colophony and gum camphor, and partly cumarone, kauri, mastic, elemi. Non-solvent for ester gum, sandarac, copals, shellac. It is miscible with water and aromatic hydrocarbons, but not with petroleum hydrocarbons or linseed oil.

The higher mono-ethers of the series have the following characteristics :—

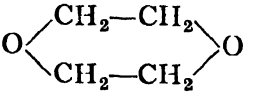
Ether.	B.P.	S.G.	R.I. at 25°.
n-Propyl	150°	·911	1·413
iso-Propyl	144°	·914	1·408
n-Butyl	171°	·919	1·418
iso-Butyl	159°	·913	1·414
iso-Amyl	181°	·900	1·420

Diethylene Glycol Mono-*n*- Butyl Ether
$C_4H_9O . CH_2 . CH_2O . CH_2 . CH_2 . OH$

Hydroxy butyloxy-ethyl ether, known commercially as " Butyl carbitol," [2] is a liquid of mild odour, which dissolves cellulose nitrate, kauri, sandarac, mastic, elemi, ester gum, cumarone, colophony, but not cellulose acetate. It partly dissolves zanzibar and shellac. It is miscible with water, linseed oil, and hydrocarbnos. B.R. 165°–230°. S.G. at 20° ·969. F.P. 172° F. (78° C). Auto-ignition temp. 228° C.

Methoxy Butyl Acetate
$CH_3O . CH(CH_3) . CH_2 . CH_2 . OOC . CH_3$

This is a high-boiling solvent available technically under the name " Butoxyl." [14] It is a colourless liquid having a weak, pleasant odour. B.R. 167°–171°. S.G. at 20° ·956. F.P. 60° C. (140° F.). E.R. 75. It is a solvent for cellulose nitrate, cellulose ethers, ester gum, gutta percha, vinyl and other resins and oils, but not for cellulose acetate or rubber. It has a high tolerance for diluents. It is soluble in water to the extent of nearly 10%, but will only dissolve traces of water.

Dioxane. 

Dioxane, or 1·4 di-ethylene di-oxide, was originally produced as an unwanted by-product in the process for manufacturing the ethers of ethylene glycol and of diethylene glycol. It results by the loss of two molecules of water from two molecules of glycol, and is a di-ether. It is made by polymerising ethylene oxide with caustic alkali or by distilling ethylene glycol with phosphoric acid, sulphuric acid, zinc chloride or benzene sulphonic acid ; the process is made continuous by adding fresh glycol to the boiling mixture to replace that which is used up.[15]

Physical Characteristics : $S.G._{20}$ 1·0338. M.P. 11·8°. B.P. 101·3° C. V.P. 27 mm. at 20° C. L.H. 86. S.H. ·41. R.I. 1·423. F.P. 52° F. (11° C.). A commercial product is available [18] having : B.R. 94°–110°. $S.G._{20}$ 1·030. F.P. 5° C. (41° F.). Vis. 1·2 at 25°. Dielec. const. 2·2. S. ten. 37 at 25°. A colourless liquid with an odour of butyl alcohol. It is dangerously toxic. Dioxane has been added to the list of poisonous substances coming within the schedule of industrial diseases under the Workmen's Compensation Act, Home

Office Statutory Rules and Orders, 1934, No. 551. Miscible with water, petroleum, and aromatic hydrocarbons, castor and linseed oils, and most organic solvents. Stable to light but forms a peroxide in air.

The following constant-boiling mixtures are known :—

Dioxane 80%.	Water 20%.	B.P. 87·0° C.
,, 40%.	*m*-Xylene 60%.	,, 136·0° C.
,, 2·5%.	*Iso*-Amyl-alcohol 97·5%.	,, 131·3° C.

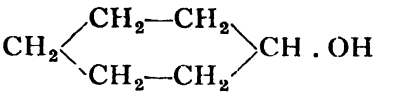
Dioxane dissolves ester gum, polystyrene, glyceryl phthalate and vinyl resins, shellac, cumarone, manila, dewaxed dammar, pontianac, elemi, kauri, sandarac, mastic, guaiac resins,[16] rubber, gutta percha resin, plextol, cellulose acetate with an acetyl content of 36% or more, ethyl and benzyl cellulose, and, in the presence of alcohol, cellulose nitrate containing 10·8 to 13·8% of nitrogen, water increases the solvent properties of dioxane for both cellulose acetate and nitrate.

References

[1] *Cf.* D.R.P. 404999 (1919).
[2] Carbide and Carbon Chemicals Company, N.Y., U.S.A.
[3] *Paint, Oil and Chem. Review*, April, 1928, p. 11.
[4] Brit. Pat. 286850. *Cf.* Brit. Pat. 365589.
[5] U.S. Pat. 1614883.
[6] Brit. Pat. 271169 ; F.P. 610282.
[7] C.P. 265191 (1926) ; B.P. 322037 ; B.P. 354357 ; B.P. 367353.
[8] Brit. Pat. 236379 ; D.R.P. 403643 (1921). *Cf.* B.P. 374864.
[9] Brit. Pat. 402438 ; U.S.P. 1954336.
[10] American Society for Testing Materials, 260 S. Broad Street, Philadelphia.
[11] D.R.P. 403643 ; Brit. Pat. 236379.
[12] *Ind. Eng. Chem.*, 1927, p. 474.
[13] U.S. Pat. 1633927.
[14] I.G. Farbenindustrie A.G., Frankfurt.
[15] U.S. Pat. 1681861 (1928).
[16] Brit. Pat. 275653.
[17] Brit. Pat. 311671 ; 328083.
[18] H.M. Stationery Office, London, W.C.2.

CHAPTER VI

CYCLOHEXANE DERIVATIVES

Cyclohexanol. 

CYCLOHEXANOL, or Hexahydrophenol, is a product obtained by the catalytic hydrogenation of phenol, and consists of a mixture of two geometric isomers. Phenol, completely freed from sulphur compounds, is treated with hydrogen gas under at least four atmospheres pressure, in the presence of a nickel catalyst, at temperatures ranging between 160°–200° C.[1] The reaction takes place in two stages, tetrahydrophenol first being formed. If the temperature be allowed to rise too high relatively to the pressure, dehydrogenation of the hydroxyl group takes place and cyclohexanone is formed; this fact forms the basis for the manufacture of cyclohexanone.

Cyclohexanol is an oily liquid, having a persistent camphoraceous, amyl-alcohol odour, strong but not highly objectionable.

Physical Characteristics: S.G. ·947. R.I. 1·465–1·466. F.P. 68° C. (155° F.). M.P. (pure) 25° C., (tech.) 10°–15°. B.P. 160° C. B.R. 159°–162°. Solubility in water 6% at 20° C. Dissolves 12% of water at 20° C. Neutral and non-phenolic. E.R. (ether = 1) 403. Vis. 1·4.

Pure cyclohexanol is not a solvent for either cellulose acetate or nitrate; technical preparations containing cyclohexanone dissolve some forms of the acetate as well as the nitrate.

It is a solvent for ester gum, glyceryl phthalate resin, benzyl abietate, mastic, shellac, cumarone, colophony, kauri, manila, bakelite A, gutta percha resin, and for basic dyes. Its solvent properties for rubber, copal, dammar and elemi are poor. It is miscible with linseed oil, petroleums and aromatic hydrocarbons. It forms the following azeotropic mixtures :—

Cyclohexanol 45%.	Furfural 55%.	B.P. 156° C.
,, 41%.	Camphene 59%.	,, 152° C.
,, 35%.	Pinene 65%.	,, 150° C.
,, 36%.	Pentachloroethane 64%.	,, 158° C.

Cyclohexanyl Acetate. $CH_3 . COO . CH\langle^{CH_2—CH_2}_{CH_2—CH_2}\rangle CH_2$

Cyclohexanyl acetate is the acetic ester of cyclohexanol, made by direct esterification. The quality of technical preparations varies considerably, and depends largely on the degree of esterification attained; good technical quality answers to the following specification: S.G. ·947–·950. F.P. 68° C. (155° F.). B.R. 170°–176°. Esters 90% min. Neutral. R.I. 1·438–1·440. It dissolves 1·4% of water at 20° C.

Cyclohexanyl acetate has a strong, stale, fruity odour resembling amyl acetate; it is non-poisonous and but slightly toxic. It is a powerful solvent for cellulose nitrate and cellulose ethers, giving viscous solutions; also for ester gum, colophony, dammar, elemi, manila, sandarac, kauri, congo, basic dyes, blown oils, plextol, raw rubber, rubber chloride, gutta percha resin, metal resinates, driers and albertols.

Methylcyclohexanol. $CH_2\langle^{CH_2—CH . CH_3}_{CH_2—CH_2}\rangle CH . OH$

Methylcyclohexanol, hexahydromethylphenol, or hexahydrocresol is a mixture of three isomeric secondary alcohols, each of which can exist in two geometric modifications, the predominating constituent being one of the ortho-members as indicated in the formula.

It is prepared by the hydrogenation of cresol in a manner similar to that for the manufacture of cyclohexanol, but technical products vary according to the relative proportions of ortho-, meta- and para-cresols present in the cresol hydrogenated.

The following are the physical characteristics of a good technical quality containing the six isomers together with traces of cyclohexanol: S.G. ·925. R.I. 1·455–1·465. F.P. 68° C. (155° F.). B.R. 170°–180° C. Solubility in water 3%.

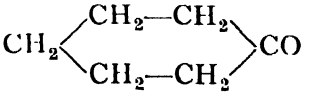
Methylcyclohexanol is an oily liquid having an odour similar to cyclohexanol.

As a solvent it is similar to, but not so powerful as, cyclohexanol.

Methylcyclohexanyl Acetate

Technical methylcyclohexanyl acetate consists of the mixture of esters obtained by the acetylation of technical methylcyclohexanol. It comes into commerce having approximately the following characteristics: S.G. ·95. F.P. 66°C. (150° F.). B.R. 172°–192° C. Esters 90% min. Neutral and anhydrous.

Its solvent properties are much the same as those of cyclohexanyl acetate, but it is somewhat slower in action; the solutions are usually more viscous and take longer to dry. Methylcyclohexanyl acetate is a good solvent for cellulose nitrate, also for colophony, ester gum, manila, mastic, benzyl abietate, elemi, dammar, kauri, bakelite, basic dyes, raw rubber, waxes and bitumen. It has some solvent action on cellulose acetate, shellac and hard copals.

Cyclohexanone. 

Obtained by the catalytic hydrogenation of phenol at high temperatures, also by the dehydrogenation of cyclohexanol, by treating a mixture of cyclohexanol and phenol with a hydrogenation catalyst,[2] and by the oxidation of this with bichromate mixture. It is a colourless liquid, having an odour suggestive of peppermint and acetone.

Physical Characteristics: S.G. ·945. R.I. 1·443–1·451. F.P. 47° C. (117° F.). R.B. 154°–156° C. Ketone-content 85% min. Chief impurity, cyclohexanol. Pure cyclohexanone has B.P. 156·5°. M.P. −45°. S.H. ·43. R.I. 1·450. Vis. 2·1. Water dissolves 8 to 9% at 20° C. It dissolves 8·7% of water at 20° C.

It is a good solvent for cellulose nitrate, yielding solutions of approximately the same viscosity as those of ethyl lactate and less viscous than those of ethylene glycol mono-ethyl ether. Its solutions of cellulose nitrate are exceptionally tolerant to dilution with toluene.

Cyclohexanone is a solvent for cellulose acetate and ethers, colophony, ester gum, kauri, elemi, manila, shellac, raw rubber, rubber chloride, bakelite, cyclohexanone formaldehyde, rezyl, vinyl, glyptal and cumarone resins, basic dyes, blown oils, bitumen, waxes and albertols. It partly

dissolves congo, dammar, and it is miscible with most organic solvents. It forms the following azeotropic mixtures :—

Cyclohexanone	55%.	Tetrachloroethane 45%.	B.P. 159° C.
,,	39%.	Trichlorhydrine 61%.	,, 160° C.
,,	56%.	Camphene 44%.	,, 151° C.

Methylcyclohexanone

This is prepared from the cresols in a manner similar to cyclohexanone. The technical product, which consists of a mixture of the three isomers, ortho-, meta,- and para-, has the following approximate characteristics : S.G. ·925–·930. R.I. 1·44–1·45. F.P. 55° C. (130° F.). B.R. 160°–175° C. Ketones 90% min. Water dissolves 3%.

A product having a ketone-content of 100% has B.R. 164°–172°. S.G. ·925. Vis. 1·8.

Methylcyclohexanone is a colourless liquid having an odour suggesting peppermint. It is a powerful solvent for cellulose nitrate, giving solutions of rather high viscosity, but very tolerant to dilution with toluene.

Its solvent properties are similar to those of cyclohexanone, but its solutions dry rather more slowly.

References

[1] *Cf.* Hilditch. "Catalytic Processes," p. 295. Chapman & Hall, 1937.
[2] Brit. Pat. 310055.

CHAPTER VII

CHLORO-COMPOUNDS

Ethylene Chlorhydrine. $Cl . CH_2 . CH_2OH$

ETHYLENE chlorhydrine, known also as glycol chlorhydrine and as 2-chloroethyl alcohol, is a colourless liquid of mild odour.

This substance is an " intermediate " involved in the manufacture of the glycol ether group of solvents and is produced from ethylene derived from producer gas, from ethyl alcohol, or from the gases arising in the cracking of petroleum. The ethylene is converted into ethylene chlorhydrine by treatment with chlorine water.[1] Water is circulated through a saturating tower wherein it is treated with chlorine gas, thus forming a solution of hypochlorous and hydrochloric acids. It then passes to a second tower and comes into contact with the ethylene which, at temperatures ranging from 0° to 20° C., combines with the hypochlorous acid to form ethylene chlorhydrine, whilst the dilute hydrochloric acid solution, which remains, is continually returned to the chlorinating tower for further treatment with chlorine until its content of hydrogen chloride reaches about $3\frac{1}{2}\%$; it is then removed. The ethylene chlorhydrine is isolated from the 8 to 10% solution thus obtained by fractional distillation.

It is also prepared in a somewhat similar fashion [2] by agitating chlorine and ethylene with water until the hydrochloric-acid content reaches about 15%, whereafter the solution is neutralised with lime and the ethylene chlorhydrine distilled out. Some difficulty is presented in isolating the chlorhydrine from the reaction mixture, one method consists in first extracting the by-product, ethylene dichloride with petroleum spirit and then the chlorhydrine with a mixture of isopropyl ether and isopropyl alcohol. Another method [4] is that of neutralising the hydrochloric acid with ammonia and then concentrating the chlorhydrine by distillation.

Ethylene chlorhydrine forms a constant-boiling mixture with water, boiling at 96° and containing 42% of the chlorhydrine by weight. The anhydrous material (96–98%) has the following characteristics : S.G. 1·20–1·21. B.R. 125°–132°. F.P. 55° C. (131° F.). B.P. 128·6. L.H. 123. R.I.

1·444 at 15°. It is clearly miscible with benzene, water, alcohol, etc. The chief impurity is ethylene dichloride.

Ethylene chlorhydrine is a solvent for cellulose acetate, and the solutions have a high tolerance for water. Cellulose acetates containing over 50% of combined acetic acid will dissolve in a mixture of equal parts of ethylene chlorhydrine and water.

Until recently ethylene chlorhydrine had been regarded as harmless, but observations and experiments have shown it to be a very dangerous material possessing unsuspected toxic properties. It has been found to be a metabolic poison with a specific effect on the nervous system; it appears also to affect the kidneys and may cause asphyxia.[5]

Monochlorhydrine. $Cl . CH_2 . CH(OH) . CH_2 . OH$

The commercial article is a mixture of two isomers of which the preponderating one is represented by the formula given above. Monochlorhydrine is not largely used in the lacquer industry, as its solvent powers are not very great; it is hygroscopic and develops acidity on prolonged contact with moisture; it also darkens with age. S.G. 1·28–1·35. B.R. 213°–228° (decomposes).

It is miscible with water and with most organic solvents, but not with hydrocarbons or vegetable oils.

Monochlorhydrine is a solvent for cellulose acetate and is useful for preparing aqueous solutions of cellulose acetate having a high tolerance for water. It dissolves glyceryl phthalate resins and has a limited solvent action on ester gum, benzyl abietate, shellac and mastic. It does not dissolve cellulose nitrate, copals, copal ester, cumarone and hard resins.

Monochlorhydrine is prepared by the partial esterification of glycerine with hydrochloric acid.

Dichlorhydrine. $Cl . CH_2 . CH(OH) . CH_2 . Cl$

Technical glycerol dichlorhydrine is a mixture of 1·3-dichloro-propanol 2 and 1·2-dichloro-propanol 3, the former preponderating. It is a colourless liquid, having a weak odour of chloroform, and is not readily inflammable.

Like other chlorhydrines, it tends to liberate hydrochloric acid in the presence of moisture and also to turn brown with age. It possesses powerful solvent properties, but its defects severely restrict its use.

Physical Characteristics : S.G. 1·34–1·38. B.R. 95% between 174° and 176°. B.P. (1·3) 174° ; (1·2) 183°. R.I. 1·47–1·48. F.P. 74° C. (165° F.). V.P. 7 mm. Dielec. const. 12. Solubility in water about 10%.

It is miscible with castor and linseed oils, aromatic hydrocarbons and most organic solvents, but not with petroleums or turpentine. Solvent for cellulose acetate, ethyl cellulose and for some forms of cellulose nitrate, for ester gum, copal ester, glyceryl phthalate resin, benzyl abietate, shellac, cumarone, mastic, elemi, dammar, manila, kauri, soft copals and caoutchouc.

It forms a constant-boiling mixture with 50% of ethyl lactate boiling at 143°, and with 61% of cyclohexanone boiling at 160°.

It is produced by the action of dry hydrochloric acid gas on glycerine.

Epichlorhydrine. $CH_2—CH—CH_2 . Cl$ (O)

Epichlorhydrine is a highly mobile, colourless liquid having an odour weaker than, but resembling, that of chloroform ; it is narcotic but not poisonous. Although it is an excellent solvent for lacquer work, it possesses the unfortunate property of liberating hydrochloric acid in contact with moisture.

It is prepared from the dichlorhydrines by the action of alkalis ; it is non-miscible with water and with petroleum hydrocarbons, but miscible with the aromatic hydrocarbons and all the usual solvents. S.G. 1·19–1·20. B.P. 117° C. M.P. –48°. R.I. 1·438. L.H. ·83. Vis. 1 at 25°. Dielec. const. 23. Elec. cond. $5·4 \times 10^{-8}$.

It is a powerful solvent for cellulose nitrate and acetate, ester gum, glyceryl phthalate resin, benzyl abietate, cumarone and soft resins ; a moderately good solvent for ethyl cellulose, shellac, mastic, kauri and manila ; it does not dissolve hard copals or copal ester. It forms the following azeotropic mixtures :—

Epichlorhydrine	23%.	*n*-Propyl alcohol 77%.	B.P. 96° C.
,,	40%.	Isobutyl alcohol 60%.	,, 105° C.
,,	81%.	Isoamyl alcohol 19%.	,, 115° C.
,,	26%.	Toluene 74%.	,, 108° C.
,,	52%.	Tetrachloroethylene 48%.	,, 110° C.

Methylene Dichloride. CH_2Cl_2

Methylene dichloride or dichlormethane is a highly volatile solvent which is produced along, with chloroform (*q.v.*), carbon tetrachloride and methyl chloride by the chlorination of methane.[6] It is a solvent for cellulose esters and is being used to raise the flash-point of lacquers.[32] Like most chlorinated paraffins, it is narcotic.

Characteristics : S.G. 1·346. B.P. 40°. V.P. 147 (0°); 230 (10°); 349 (20°); 511 (30°). S.H. ·26, L.H. 78. Dissolves 0·1–0·2% of water. Water dissolves 2·363% (0°); 2·122 (10°); 2·000 (20°); 1·969 (30°). Vis. ·43. Elec. cond. $4·3 \times 10^{-11}$. Dielec. const. 9·14.

It is a solvent for rubber, bitumen, pitch, caoutchouc, oils, waxes, vinyl acetate, plextol and other resins.

It frequently contains traces of methyl chloride, which lowers the boiling-point.

Chloroform. $CH Cl_3$

Chloroform, being of a highly narcotic nature, does not find wide application as a lacquer solvent, but it possesses very high solvent powers and has been used for special purposes such as the manufacture of art silk.

It can be made by a variety of methods, and the time-honoured one of distilling alcohol or acetone with bleaching powder is still used; a variation consists in chlorinating anhydrous alcohol with dry chlorine gas and treating the chloral hydrate thus formed with alkali.[7] It can also be made by treating acetaldehyde with bleaching powder solution.[8] A process now attaining considerable importance is the direct catalytic chlorination of methane.[9] Mixtures of methane, methyl chloride and chlorine are passed through earthenware reaction chambers at temperatures ranging from 350°–650° C., whereby mixtures of chloroform, carbon tetrachloride and methylene dichloride are obtained.

Chloroform has the following characteristics: S.G. 1·49–1·50. R.I. 1·445–1·449. B.P. 61·2°. M.P. –63°. V.P. 162. L.H. 59. S.H. ·225. Vis. ·56. Elec. cond. $<10^{-10}$. Dielec. const. 4·64. Non-inflammable. Solubility in water 0·5%.

Chloroform slowly becomes acid in the presence of light and moisture: a small quantity of alcohol is usually added to prevent this; the British Pharmacopœia specifies 2%. It

dissolves cellulose acetate, benzoate, dinaphthenate and ethyl cellulose, also rubber, gutta percha and most resins.

The following azeotropic mixtures are known :—

Chloroform 87·5%.	Methyl alcohol 12·5%.	B.P. 53·5° C.
,, 93%.	Ethyl alcohol 7·0%.	,, 59·4° C.
,, 72%.	*n*-Hexane 28%.	,, 60° C.
,, 90%.	Acetone 20%.	,, 64·7° C.
,, 22%.	Methyl acetate 78%.	,, 64·5° C.

Carbon Tetrachloride. CCl_4

Carbon tetrachloride or tetrachloromethane is one of the most widely used solvents of this group. It is a colourless, non-inflammable liquid, having an odour somewhat similar to that of chloroform ; it is dangerously toxic and generates poisonous gases, namely, phosgene, hydrochloric acid, and chlorine, when in contact with burning substances, or with water at high temperatures.

It is made from carbon bisulphide by the action of chlorine in the presence of sulphur or iodine,[10] or of sulphur chlorides [11] in iron vessels the use of which prevents the formation of the highly toxic tri-chloro-methyl-sulphur chloride ; also by the chlorination of methane or methylene chloride,[12], acetylene [34] and perchlorethylene,[35] and by passing chlorine through incandescent carbon or coke.[13]

British Standard Specification No. 575—1934. S.G. 1·600–1·608 (1·596–1·604 at 20°). B.R. up to 75·7° 2% max. ; 75·7–76·7 –95% min. Residue ·01% max. Neutral to methyl orange. Sulphur compounds ·1% max. as CS_2. Free from free chlorine. The Australian Standard is similar to the British. The material also has M.P. –23°. V.P. 91. L.H. 47. S.H. ·202. R.I. 1·460. Vis. ·96. Water dissolves ·08% at 20°. Dissolves ·008% of water at 20° C. Elec. cond. 4×10^{-18}. Dielec. const. 2·2. Dielec. strength 33,000 volts min.

It tends slowly to liberate hydrochloric acid on contact with water, but has no action, when dry, on iron, nickel or aluminium ; it attacks copper and lead slightly.

It dissolves some varieties of cellulose acetate and di-naphthenate, but not the nitrate ; it is a good solvent for ethyl cellulose, cumarone, benzyl resin, mastic, polystyrene, dammar, rosin, albertols, bitumen, thio-urea resins and rubber heptachloride, and partly dissolves sandarac, soft copals,

kauri and vinyl resin. It does not dissolve shellac, accroides, or hard copal.

The following azeotropic mixtures are known :—

Carbon tetrachloride	57%.	Ethyl acetate 43%.	B.P. 74·8° C.
,,	84%.	Ethyl alcohol 16%.	,, 64·9° C.
,,	79%.	Methyl alcohol 21%.	,, 55·7° C.
,,	89%.	*n*-Propyl alcohol 11%.	,, 72·8° C.
,,	94·5%.	*Iso*-butyl alcohol 5·5%.	,, 75·8° C.
,,	86%.	*Iso*-propyl alcohol 14%.	,, 67·0° C.
,,	71%.	Methyl ethyl ketone 29%.	,, 73·8° C.

sym.-Dichlorethane. $CH_2Cl . CH_2Cl$

Sym.-dichlorethane or ethylene dichloride is not to be confused with dichlorethylene.

It is a colourless mobile liquid with an odour similar to that of chloroform ; it is toxic and produces dangerous physiological effects like those of chloroform. Air saturated at 20° C. with di-chlorethane contains about 10% by volume ; the odour of di-chlorethane is quite marked at ·1%.

In its manufacture by the direct chlorination of ethane, the two gases, in equal volumes, are led over activated carbon at 100°–300° C., ethyl chloride and trichlorethane are also formed in small quantities.[33] Also made from ethylene and chlorine by treatment with calcium chloride,[14] or with the chloride of iron, copper, or antimony at 30°–120° C.[15], or by passing ethylene gas into liquid chlorine at low temperature. In the manufacture of ethylene glycol it is formed as an intermediate product. It is slowly hydrolysed by water, and causes slight corrosion of metals.

S.G. at 20°, 1·250–1·257. B.R. 80°–85°. V.P. at 20° 65 mm. S.H. at 30° 0·3054. L.H. 88. B.P. 83·5°. F.P. 17° C. (63° F.), but burns only with difficulty. M.P. –36°. R.I. about 1·444. Vis. ·83. S. ten. 37 at 25°. Dielec. const. 10.

Solubility in water, 0·1% at 20°. Dissolves 0·8% of water at 20°. It will not dissolve cellulose nitrate or acetate except after admixture with alcohols, glycol ethers or ethyl acetate. It is a solvent for rubber, and partly for soft copals, sandarac, mastic, elemi, guaiac, japan wax, lead linoleate. It readily dissolves manila, dammar, cumarone, ester gum, camphor gum, rosin, gum lac, bakelite, albertols, plextol, vinyl and glyceryl phthalate resins, polystyrene, zinc resinate, benzyl abietate, benzyl cellulose, ethyl cellulose, turpentine, paraffin wax, gilsonite, mineral oils, cotton-seed oil, castor oil, linseed

oil. It does not dissolve congo, kauri, pontianac, shellac, beeswax or carnauba wax.

sym.-**Tetrachlorethane.** $CHCl_2 . CHCl_2$

Formerly called acetylene tetrachloride, and known under the name of " Westron," [23] this solvent is a colourless mobile liquid having an odour resembling those of carbon tetrachloride and chloroform. It is the most powerful solvent of its class.

Tetrachlorethane, like most of the substances of this class, is dangerously toxic [16] and must only be employed in enclosed apparatus or in well-ventilated spaces. It causes jaundice and enlargement of the liver, the diseases being notifiable under the Factory and Workshop Act, section 73, Order No. 1170 of November, 1915.

It attacks iron, copper, nickel, and lead slightly, and aluminium vigorously. In the presence of moisture it slowly liberates hydrochloric acid. It is non-inflammable and is useful for reducing the inflammability of lacquers.

S.G. 1·600–1·602. R.I. 1·494. B.R. 140°–150°. B.P 146° V.P. at 20° 11 mm. S.H. at 20° ·268. L.H. 55 S.P. –44° C. Vis. 1·6 at 25°. Dielec. const. 7·8. Water dissolves ·3% at 25°.

Tetrachlorethane is a solvent for cellulose acetate and nitrate, ester gum, bitumen, waxes, resins, tar, pitch, colophony, rubber, rubber chloride, caoutchouc and oils. It dissolves about 1% of sulphur.

It is prepared by the interaction of acetylene and chlorine, but the direct reaction is dangerously explosive. In order to moderate the reaction, it is sometimes conducted in a cooled bed of sand or by passing alternately acetylene at 60°–80° and chlorine at 80°–100° into antimony pentachloride,[17] or by passing the gases separately but simultaneously over a catalyst composed of iron turnings mixed with quartz and sprinkled continuously with tetrachlorethane.[18]

Another system consists in circulating a dilute solution of antimony chloride in tetrachlorethane between two vessels in one of which the liquid is treated with acetylene and in the other chlorine. A double compound of acetylene and antimony chloride forms in the first vessel and reacts with the chlorine in the second vessel to form tetrachlorethane and reliberate the antimony chloride.

The following azeotropic mixtures are known :—

Tetrachlorethane 91%.	Glycol 9%.	B.P. 145° C.
,, 45%.	Cyclohexanone 55%.	,, 159° C.
,, 68%.	Isoamyl acetate 32%.	,, 150° C.

Tetrachlorethane has been known as " Tetraline," but this name has fallen into disuse, since it caused confusion with the name " Tetralin " applied to tetrahydronaphthalene.

Pentachlorethane. $CHCl_2 . CCl_3$

This is a colourless, non-inflammable, toxic liquid prepared by the catalytic chlorination of trichlorethylene, and by the action of chlorine on sym.-tetrachlorethane in actinic light.[19] Also by boiling tetrachlorethane with zinc dust and water. S.G. 1·685–1·709. R.I. 1·5035. B.P. 162°. V.P. at 22° 2·7. S.H. at 20° 0·2. L.H. 44. S.P. —22° C. Vis. 2·2 at 25°. Dielec. const. 3·6. Water dissolves ·05% at 25°.

It is a good solvent for cellulose acetate and for some resins. The following azeotropic mixture is known : Pentachlorethane 85%, glycol 15%, B.P. 154·5°.

***sym.*-Dichlorethylene.** $CHCl = CHCl$

Sym.-dichlorethylene, sometimes termed acetylene dichloride, is not to be confused with ethylene dichloride, which is sym.-dichlorethane. It is a colourless liquid, toxic, but apparently not dangerously so. The cold liquid is non-inflammable, but the hot vapour can be ignited, it burns with a cold flame which extinguishes itself ; in practice there is no danger from fire. The commercial product is a mixture of two stereoisomers, the transisomer, present to the extent of about 40%, boils at 48°, and the cis. at 60° C. It slowly liberates hydrochloric acid on contact with water, but has no action on metals when anhydrous.

Dichlorethylene is manufactured by the partial and carefully regulated chlorination of acetylene, a mixture containing 10% of chlorine being heated to 40° C.[20] ; also by the interaction of acetylene and hydrogen chloride at ordinary temperature in the presence of an oxidising agent in a gaseous form, such as nitrogen peroxide, formic acid, formaldehyde, iodine, or oxygen.[21] It cannot be heated with alkalis, as this treatment causes the liberation of the spontaneously explosive substance, chloroacetylene.[22]

S.G. 1·25–1·278. B.R. 48°–60°. V.P. at 20° about 205 mm. R.I. 1·505. S.H. at 20° 0·27. L.H. 71. Vis. ·4 at 25°. Dielec. const. 6·7. Burns only with great difficulty. Water dissolves ·6% at 25°.

It dissolves cellulose acetate, oils, shellac, tars, waxes and resins. It is the best solvent for rubber. Insoluble in water.

Trichlorethylene. $CHCl = CCl_2$

Trichlorethylene, or ethylene trichloride, is known commercially as " Westrosol." [23]

It is a colourless mobile toxic liquid with an odour resembling that of chloroform. It is stable to moisture, but not to light ; it attacks iron slightly, but not copper, lead, aluminium or nickel. Small quantities of stabilisers are sometimes added to prevent the slight decomposition to which the corrosive action is due.

Trichlorethylene is manufactuerd from tetrachlorethane by boiling with lime water or with water and zinc, iron, or aluminium ; also by passing tetrachlorethane over thorium oxide heated to 390° (maximum),[24] or into the chloride of a tetravalent metal [25] at 300° ; other methods consist in refluxing tetrachlorethane with water through which ammonia is passed violently,[26] and in treating tetrachlorethane with calcium oxide and a non-caustic soda compound.[27] A recent method[28] is that of the passage of tetrachlorethane at high speed over pumice, charcoal, silica gel, etc., at 500°.

British Standard (Technical and Stabilised) 580—1934. S.G. 1·469–1·475 (1·461–1·468 at 20°). B.R. 86·2–87·2°, 95% min. (technical), 86°–88°, 95% min. (stabilised). Residue ·01% max. Acidity ·002% max. as HCl. Free from free chlorine. The material also has R.I. 1·478. V.P. 58. S.H. ·223. L.H. 57. M.P. –86. B.P. 86·9. Vis. ·58. S. ten. 32. Cub. exp. ·0011. Dielec. const. 3·4. Water dissolves ·2% at 25°. Dissolves ·03% of water at 25°.

It forms the following azeotropic mixtures :—

Trichlorethylene 64%.	Methyl alcohol 36%.	B.P. 60·2° C.
,, 73·%	Ethyl alcohol 27%.	,, 70·9° C.
,, 81%.	*iso*-Butyl alcohol 19%.	,, 85·4° C.
,, 82%.	*n*-Propyl alcohol 18%.	,, 81·8° C.
,, 86%.	*Iso*-Propyl alcohol 14%.	,, 74·0° C.

It is a solvent for cumarone, rubber, rubber chloride, bitumen, mastic, plextol, elemi, vinyl resin, colophony, grease,

sulphur, but will not dissolve cellulose nitrate, shellac or manila. It will dissolve some forms of cellulose acetate, especially in the presence of cyclohexanol. If mixed with methyl or ethyl alcohol it will dissolve ethyl cellulose. It does not dissolve linseed oil. It is a useful low-boiler for reducing the inflammability of lacquers.

Perchlorethylene. $CCl_2 : CCl_2$

This colourless non-inflammable liquid is sometimes termed tetrachlorethylene. It is prepared from pentachlorethane by treatment with mild alkalis.

S.G. 1·624–1·632. R.I. 1·502–1·506. B.R. 119°–122°. B.P. 120·8°. V.P. at 20° 15. L.H. 50. S.H. at 20° 0·216. S.P. —19° C. Vis. ·9. Dielec. const. 2·4. Water dissolves ·04% at 25°. Dissolves ·01% of water at 25°.

Perchlorethylene forms the following azeotropic mixtures :—

Perchlorethylene 19%.	Ethyl alcohol 81%.	B.P.	78° C.
,, 46%.	*n*-Propyl alcohol 54%.	,,	94° C.
,, 60%.	*iso*-Butyl alcohol 40%.	,,	103° C.
,, 81%.	*iso*-Amyl alcohol 19%.	,,	116° C.
,, 48%.	*a*-Epichlorhydrine 52%.	,,	110° C.

It is a toxic liquid, stable to moisture, does not attack metals, and is a solvent for cellulose acetate.

Monochlorbenzene. $C_6H_5 . Cl$

Monochlorbenzene, or chlorbenzol, is a colourless mobile liquid, having a mild almond odour, also a mild narcotic effect, but it is relatively harmless and less toxic than benzene. It is prepared by the chlorination of benzene in the presence of chlorine-carriers, such as iron [29] or aluminium, also by the action of sulphuryl chloride in the presence of similar catalysts.[30] S.G. 1·112. B.P. 132°. R.I. 1·525. V.P. at 20° 8·7 mm. F.P. 83° F. (28° C.). Vis. ·8. Dielec. const. 5·6.

It is not miscible with water and does not develop acidity. It is miscible with most organic solvents and dissolves ethyl cellulose, soft copals, dammar, bakelite A, rubber, colophony, plextol, vinyl and other resins. It is useful for producing lacquers, which dry with a matt or " crackle " surface.

It forms the following azeotropic mixtures :—

Chlorbenzene 64%.	Isoamyl alcohol 36%.	B.P.	124·3° C.
,, 37%.	*n*-Butyl alcohol 63%.	,,	107·2° C.
,, 20%.	*n*-Propyl alcohol 80%.	,,	96·5° C.

***sym.*-Dichlorethyl Ether.** $Cl . CH_2 . CH_2 . O . CH_2 . CH_2 . Cl$

Symmetrical or $\beta\beta'$-dichlorethyl ether is a colourless liquid, having an odour like that of ethylene dichloride (*sym.*-dichlorethane). It is prepared by treating ethylene glycol chlorhydrine (β-chlorethyl alcohol) with sulphuric acid.

Characteristics : B.P. 178°. M.P. —51·7°. S.G. at 20° 1·22. R.I. 1·457. V.P. 0·73 at 20°. S.H. 0·369. L.H. 64. F.P. 131° F. (55° C.). I.P. 369° C. S. ten. 42. Vis. 2 at 25°. It dissolves 0·1% of water at 20° C.

It is a solvent for mastic, cumarone, benzyl abietate, ester gum, zinc resinate, paraffin wax, gum camphor, castor, linseed, cotton-seed and other fatty oils, turpentine, albertols, rezyls, bakelite R 325, and glyceryl phthalate resins. It does not dissolve rosin, manila, dammar, kauri, congo, sandarac, pontianac, shellac, vinyl resin, beeswax, carnauba wax or japan wax. It dissolves ethyl cellulose, but not other cellulose ethers or esters except in the presence of 10–30% of alcohol. It is miscible with aromatic but not with paraffin hydrocarbons. B.P. 116°. S.G. at 20° 1·213. R.I. 1·457.

It is not to be confused with symmetrical *aá-dichlorethyl ether*, which is made by the action of hydrochloric acid on acetaldehyde.

1-2 Dichlorpropane. $CH_2Cl . CHCl . CH_3$

A colourless liquid known also as propylene dichloride. It has solvent and toxic properties similar to those of dichlorethane. S.G. 1·56 at 20°. B.P. 96°. R.I. 1·407. F.P. 21° C. (70° F.). L.H. 72. S.H. ·334. S. ten. 31. V.P. 36. M.P. —80° C. Cub. exp. ·0011. Vis. 8·6. Exp. lim. 3·4 to 14·5.

Amyl Chloride. $C_5H_{11} . Cl$

A technical product is now available [35] consisting of a mixture of :—

n-Amyl chloride.	B.P. 106·6° (740).	S.G. ·9013 (0°)
iso-Amyl chloride.	„ 99·1° (760).	„ ·8928 (0°)
3-Chloropentane.	„ 103–105° (760).	„ ·916 (0°)
2-Chloropentane.	„ 96–97° (746).	„ ·912 (0°).
1-Chloro-2-methyl butane.	„ 97·6–99° (760).	„ ·8812 (17·5°)
tert-Amyl chloride.	„ 85·7° (760).	„ ·889 (0°)

It is a solvent for waxes, oils, tars, rubber and resins, is non-miscible with water, has a specific gravity of 0·88 at 20°, and a boiling range of 95% between 85° and 109°.

n-Amyl chloride, B.P. 102°–110° (95%). S.G. ·885 at 20° is also available.[31]

Dichloropentane

Also known as amylene dichloride is a light straw-coloured solvent for oils, resins, bitumens, raw rubber and vulcanised rubber. It has S.G. 1·07–1·08 at 20°. Acidity ·025%. H.Cl max. B.R. 130°–200° 95%. F.P. 97° F. I.P. 130° F. S. ten. 31·8. L.H. 68. S.H. ·369. Vis. 1·6 at 25° C. K.B.V. 67. Insol. water. It forms a psuedo azeotrope with 34% of water.

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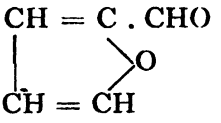
CHAPTER VIII

FURFURALS

Furfural.



FURFURAL, or furfurol as it is inaccurately termed, has been known for over a hundred years, having been discovered by Doebereiner in 1830, in the products of the destructive distillation of sugar. Its preparation from bran, straw, wood and other carbohydrate material is also a matter of history, and it was not until quite recent times that its manufacture on an industrial scale was undertaken. The raw material from which it is prepared is oat hulls, which was formerly a waste product obtained in the manufacture of rolled oats.[1] These hulls contain from 32 to 36% of pentosans, together with about 35% of cellulose and 10 to 15% of lignin ; they are digested in copper-lined steel autoclaves, with about one-third of their weight of 5% sulphuric acid. The autoclaves are fed with steam at 60 lbs. per sq. in., the steam carries off the furfural and small quantities of other volatile substances, the maximum content of furfural reached in the vapour during the operation being about 10%. This steam is passed into copper fractionating columns, whence crude furfural containing about 16% of water is obtained in a yield of somewhat more than 10% by weight of the hulls.

This crude furfural is deprived of its water by passing it along a volute spiral baffle enclosed in a flat pan, a space being left between the top of the spiral and the roof of the pan, by means of which steam can escape ; a steam-pipe, carrying steam at 100 lb. pressure per sq. inch, lies in the trough of the spiral, while the crude furfural is fed into the trough at its centre and caused to flow along the steam-pipe to the outlet at the edge.

The dehydrated crude furfural can be decolorised and purified by vacuum distillation, the product slowly assumes its brown colour again, but the colouration is inhibited by the addition of ·25% of hydroquinone or paraldehyde.

Pure furfural has the following characteristics : S.G. 1·1598 at 20°. R.I. 1·5261. B.P. 161·7°. S.P. −36·5°. F.P.

56° C. (133° F.). Two grades are available technically [1]: Refined, S.G. 1·159–1·161 at 20°. B.R. 159°–162°. F.P. 56. Purity 99%. Technical, S.G. 1·158–1·160 at 20°. B.R. 158°–162°. Purity 98·5. Acidity 0·33% as acetic acid. Furfural mixes in all proportions with most organic solvents excepting petroleums, in which it is but slightly soluble.

The mutual solubilities of furfural and water are given in the following table [7]:—

Temperature, °C	Furfural % weight in	
	Water layer.	Furfural layer.
10	7·9	96·1
20	8·3	95·2
40	9·5	93·3
60	11·7	91·4
80	14·8	88·7
97·9	18·4	84·1

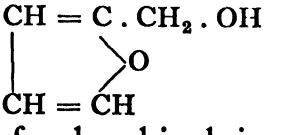
Furfural dissolves cellulose nitrate,[3] acetate, [4] and nearly all known cellulose esters and ethers, but is rather slow in its action; its solvent properties are increased by its admixture with alcohols and with benzene. It dissolves ester gum, cumarone, bakelites and glyceryl phthalate resins, but is not a good solvent for resins in general, linseed oil, or rubber, and is not compatible with gasoline.

Solutions of cellulose nitrate in furfural have viscosities approaching those in ethyl lactate and have but moderate toleration for dilution with toluene or butanol. The odour of furfural is strong and somewhat tiresome, although not definitely unplesant; the vapour is slightly toxic in high concentrations.

The following azeotropic mixtures are known:—

Furfural 38%.	Pinene 62%.	B.P. 143° C.
,, 55%.	Cyclohexanol 35%.	,, 156° C.
,, 40%.	Camphene 60%.	,, 147° C.

Furfuryl Alcohol.



This alcohol, known also as furyl carbinol, is a colourless, almost odourless, syrup obtained by the partial hydrogenation

of furfural ; it has the following characteristics : S.G. at 20° 1·133. R.I. 1·487. B.R. 169°.

It yields viscous solutions of cellulose nitrate,[6] gels cellulose acetate and dissolves ester gum, cumarone, sandarac, mastic, kauri, shellac, pontianac. It does not dissolve congo, guaiac or dammar. It is miscible with water and many of the usual organic solvents with the exception of some petroleum hydrocarbons and vegetable oils.

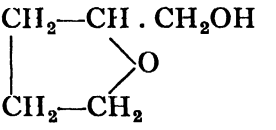
It is said to be non-poisonous but prolonged contact with the skin should be avoided.

Furfuryl Acetate

This is obtained by the direct acetylation of furfuryl alcohol ; it has the following physical properties : S.G. 1·1175 at 20°. R.I. 1·4627. B.P. 176° C.

It yields solutions of cellulose nitrate, the viscosities of which approximate to those in ethyl lactate, and which are moderately tolerant to dilution with aromatic and paraffin hydrocarbons. It is a solvent for ester gum and cumarone.

Tetrahydro Furfuryl Alcohol.



This is another product arising from the partial, but more complete, hydrogenation of furfural, it having been found possible, but not economic, to hydrogenate as far as *n*-amyl alcohol.

Tetrahydro furfuryl alcohol is a saturated substance and does not discolour with age like the unsaturated furfurals. Its physical characteristics are : S.G. 1·055 at 20°. R.I. 1·452. B.R. 170°–178°. F.P. 75° C. (167° F.).

It dissolves cellulose nitrate, yielding solutions having viscosities about double those of corresponding concentration in ethyl lactate ; these solutions have high tolerances for aromatic hydrocarbons but are not readily compatible with the paraffins. Tetrahydro furfuryl alcohol is a solvent for rubber chloride, ethyl cellulose, benzyl cellulose, cellulose acetate, rosin, ester gum, cumarone, sandarac, pontianac, guaiac, vinyl acetate resin, mastic, kauri, soft copals, shellac and water. Probably non-toxic.

Tetrahydro furfuryl acetate is a solvent for cellulose nitrate.

The furoic or pyromucic esters all dissolve ester gum,

Furfural Derivatives of Less Importance [5, 7]

	S.G. at 20°.	R.I.	B.P.
Methyl furoate . .	1·1786	1·4869	181° C.
Ethyl furoate . .	1·1774	1·4782	197° C.
n-Propyl furoate . .	1·0745	1·4750	211° C.
n-Butyl furoate . .	1·0555	1·4740	233° C.
Isoamyl furoate . .	1·0335	1·4720	232° C.
Amylene glycol 1 . 2 .	0·9802	1·4413	210° C.
Amylene glycol 1 . 5 .	0·9938	1·4499	237° C.
Furane . . .	0·937	1·4216	31° C.
n-Butyl furfuryl ether .	0·955	—	190° C.

cumarone, and cellulose nitrate, but not congo, guaiac, dammar, sandarac, mastic, kauri, pontianac or shellac. The solutions of cellulose nitrate have high viscosities, whilst their tolerance for toluene is about the same as that of diacetone alcohol; for butyl alcohol and paraffins it is high, excepting methyl furoate, which is incompatible with paraffins. The esters are all insoluble in water and tend to darken with age.

Furoic acid or pyromucic acid is obtained by the limited oxidation of furfural.

n-Butyl furoate is now available technically, having S.G. 1·054 at 20°. B.R. 226°–229°. Esters 99–100%. Its odour is similar to that of amyl salicylate.

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CHAPTER IX

PLASTICISING SOLVENTS

Acetophenone. $C_6H_5 . CO . CH_3$

THIS substance has been used as a softening solvent. It has powerful solvent properties, but its strong, though pleasant odour and high cost militate against its use. It has a decided hypnotic action. Its characteristics are :—S.G. at 20° 1·0295. M.P. 19°–20°. B.R. 200°–202°. R.I. 1·534–1·537. Dil. rat. toluene 2·7. Vis. 1·8. F.P. 221°F. (105° C.).

It is a powerful solvent for cellulose nitrate and rapidly gels cellulose acetate. It also dissolves ethyl celluose, shellac, cumarone, glyceryl phthalate resin, polystyrene, and vinyl resin. It yields strong flexible and resplendent films with the cellulose esters. It is miscible with linseed and other oils and with hydrocarbons, but not with water.

Diacetin.

$$\begin{array}{l} CH_2 . OOC . CH_3 \\ | \\ CH . OH \\ | \\ CH_2 . OOC . CH_3 \end{array}$$

Diacetin, or glyceryl diacetate, is a mixture of the isomeric esters of which the one shown above preponderates. It is occasionally employed when a soft film is required, especially in the case of cellulose acetate films, and also for the purpose of incorporating dyes of glyceryl phthalate resin.

It is a solvent for cellulose acetate and nitrate, shellac, glyceryl phthalate resin. It partly dissolves mastic, benzyl abietate, and castor oil. It does not dissolve ester gums, cumarone or copals, and is not miscible with linseed oil, paraffin hydrocarbons or toluene. It is miscible with benzene and with water and is hydroscopic. *Characteristics :* S.G. 1·186. B.P. about 259°. F.P. 295° F. R.I. 1·44. Dil. rat. toluene 0·35. It frequently contains triacetin and monacetin.

Triacetin.

$$\begin{array}{l} CH_2 . OOC . CH_3 \\ | \\ CH . OOC . CH_3 \\ | \\ CH_2 . OOC . CH_3 \end{array}$$

Triacetin, or glyceryl triacetate, is one of the most widely used and valuable plasticisers. It possesses high plasticising

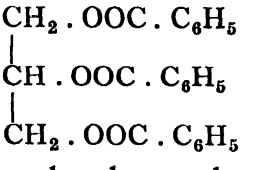
power for cellulose nitrate, cellulose acetate and ethyl cellulose, for all of which it is a good solvent, and in which it can be incorporated in any proportion without causing cloudiness. It tends to yield soft films if used in proportions exceeding about 66% of the weight of the cellulose ester. It is particularly useful when it is desired to incorporate glyceryl phthalate resins, vinyl acetate and vinyl acetal resins, cyclohexanone formaldehyde resin or copal ester with the cellulose esters. It partly dissolves ester gum, shellac, cumarone, mastic and hard copals, and is a moderate solvent for benzyl abietate, blown castor oil and linoxyn, but not rubber chloride. It is non-miscible with castor oil, linseed oil or petroleum hydrocarbons, but is completely miscible with aromatic hydrocarbons. It is non-hydroscopic. Water dissolves ·6% by weight. Triacetin dissolves 3·67% of water at 18° C.

B.E.S.A. Specification,[1] 2*D*11 : S.G. 1·16–1·17. Esters 97% min. Acidity 0·1% max. Clearly miscible with benzene ; colourless.

Its B.P. is about 258°. F.P. 270° F. (133° C.). R.I. 1·431.

Dil. rat. cellulose nitrate 2·5 benzene, 0·9 toluene, 1·0 butanol. Cellulose acetate 0·4 benzene, 1·3 ethanol, 0·7 butanol. Vis. 22.

Glyceryl Tribenzoate.



This solid plasticiser is an odourless, almost white, crystalline substance, and is soluble in all the usual anhydrous solvents with the exception of petroleums. M.P. about 71°. S.G. 1·25.

With cellulose nitrate it yields very hard, glossy but brittle films in proportions up to 150% by weight of the cellulose nitrate.

It has been used for cellulose acetate, with which it yields elastic films in proportions of up to 20%.

Mixed acetic and benzoic esters of glycerine have also been used as plasticisers.[3]

Triphenyl Phosphate. $(C_6H_5 . O)_3PO$

The plasticising properties of this ester are similar to those of tricresyl phosphate. It is a white crystalline solid substance,

and is held by some to be unsuitable as a permanent plasticiser because of the possibility of it crystallising out of the film. This is only true if it be employed by itself in excessive proportions, but a second plasticiser, even in quite small quantities, will prevent it crystallising, a suitable substance being di-amyl phthalate.

Triphenyl phosphate can be used with cellulose nitrate in proportions up to 100% of the weight of the latter, large doses tend to reduce the inflammability of films. It is not a satisfactory plasticiser for the acetate, and if used it should be mixed with di-amyl phthalate, triacetin, benzyl alcohol, or amyl tartrate. If the proportion of triphenyl phosphate used be in excess of 10% of the cellulose acetate it tends to yield cloudy films. It is a plasticiser for di-ethyl cellulose, di-benzyl cellulose, cellulose stearate, laurate and oleate, vinyl acetyl resin, and shellac. the water-resistance of which it increases. It is a stable substance, and can be obtained commercially in a high state of purity.

B.E.S.A. Specification, 4*D*12 [1]: M.P. 45°–48°. Acidity 0·01% max. (as NaOH). Ash 0·05% max. Clearly soluble in chloroform. Free from phenol, chlorides, sulphates, and metallic phosphates.

B.P. about 410° C.; completely soluble in amyl acetate, acetone, benzene. F.P. 235° C. (450° F.). Dil. rat., benzene 4·5, butanol 10·5. Insoluble in water.

Tricresyl Phosphate. $(CH_3 . C_6H_4 . O)_3 . PO$

Known also as tri-tolyl phosphate and T.C.P. This substance shares with triacetin and di-butyl phthalate the honour of being the most widely used plasticiser. There are no less than ten possible isomers of tricresyl phosphate, depending on the presence of ortho-, meta- and para-cresol in the cresol used. The isomer most commonly found in commerce is the triortho-cresyl phosphate, which is a crystalline substance of M.P. 18° C. and SG. 1·185—1·189, but the presence of small quantities of other isomers renders the commercial substance liquid at ordinary temperatures, and also lowers the specific gravity and viscosity.

The *A.S.T.M. Specification D*363·36 [2] requires S.G. 1·160–1·180 at 20°. Volatile matter ·2% max. Free phenols ·05% max. Esters 99% max. Acid value ·1 max. Must withstand the permanganate test for 30 mins. Clearly miscible

with 19 vols. gasoline. The material also has B.R. 430°–440°. F.P. 230° C. (446° F.). M.P. about –35°. R.I. 1·560–1·562. S.G. 1·180–1·186 at 15°. Dil. rat. toluene 3·3, benzene 4·5, butanol 10·5. S. ten. 45. Vis. 265 (10° C.), 160 (15° C.), 106 (20°).

The pure meta isomer is liquid at ordinary temperatures, while the pure para isomer is a solid. M.P. 78°.

Tricresyl phosphate is an exceptionally stable ester ; when quite pure it is practically non-volatile and odourless, and does not develop acidity, even under highly adverse conditions. It has a powerful solvent action on cellulose nitrate and acetonitrate, but little on cellulose acetate. It plasticises di-ethyl and di-benzyl cellulose, cellulose stearate, polystyrene, methyl methacrylate, polyvinyl chloride, acetate and acetal resins. rubber chloride. It is a good solvent for ester gum, colophony, copal ester, benzyl abietate, cumarone, cyclohexanone, formaldehyde resin, glyceryl phthalate resin ; it is a moderately good solvent for shellac mastic and rubber chloride, and will dissolve hard copals on prolonged heating at high temperature. It renders shellac waterproof and also improves its adhesive properties. It serves as a good flux in which to run copals. It is clearly miscible with castor, olive, nut and linseed oils and with most of the hydrocarbons, but is non-miscible with water. It dissolves 0·2% of water at 25° C., and water dissolves 0·2% of tricresyl phosphate at 25° C.

Tricresyl phosphate diminishes the inflammability of cellulose nitrate films. It may be used in quantities up to 100% of the weight of cellulose nitrate, and up to 10% of cellulose acetate. It permits a high polish to be obtained and imparts permanent elasticity.

The stickiness sometimes engendered by ester gum may be counteracted with tricresyl phosphate. When taken by the mouth tricresyl phosphate causes chronic paralysis of the limbs.

The mixed esters, such as monophenyldicresyl phosphate and diphenylmonocresyl phosphate, have also been used as plasticisers.

Tri-ethyl Phosphate. $(C_2H_5O)_3PO$.

A colourless liquid having a mild odour resembling that of apples. It is miscible with most organic solvents and with water, which hydrolyses it slowly. It dissolves cellulose

nitrate and acetate and tends to diminish inflammability. S.G. 1·068–1·072 at 20° . R.I. 1·406. B.P. 215°.

Tri-butyl Phosphate. $(C_4H_9O)_3PO$

Tri-butyl phosphate is an odourless, colourless liquid, fast to light. It is a powerful solvent for cellulose nitrate and lowers the viscosity of its solutions ; it also dissolves cellulose acetate, ethyl cellulose and shellac. It tends to cause cellulose nitrate films to develop acidity and brittleness on exposure.

Characteristics : S.G. ·980–·985. R.I. 1·424–1·426. B.P. 289° (decomp.). F.P. 160° C. (320° F.). It dissolves 2·6% of water at 25° C. and water dissolves 0·6% at 25° C It diminishes the inflammability of cellulose nitrate. Dil. rat. toluene 24.

Tri-chlorethyl Phosphate. $(Cl . C_2H_4O)_3PO$

This is a non-inflammable plasticiser for cellulose acetate, nitrate and ethers, and solvent for resins and rubber chloride. It is a colourless liquid of low viscosity. S.G. 1·42–1·46. R.I. 1·47–1·48. B.R. 210°–220° at 20 mm. F.P. 225° C. Acidity ·01% max. HCl. Insoluble in water but soluble in all the usual organic solvents.

Tri-chlor-phenyl Phosphate. $(Cl . C_6H_4 . O)_3PO$

A colourless liquid having S.G. 1·34. R.I. 1·576. It is compatible with cellulose acetate in proportions up to 50% ; less than 15% is sufficient to render it completely non-inflammable ; it is also compatible with cellulose nitrate and polyvinyl chloride. It imparts high water resistance to films.

It is miscible with aromatic hydrocarbons, alcohols, esters and ketones but not with petroleum hydrocarbons of low aromatic content.

Butyl Oleate. $CH_3 . (CH_2)_7 . CH : CH . (CH_2)_7 . COO . C_4H_9$

Butyl oleate is occasionally used for the purpose of imparting water-resisting and high-polishing properties to cellulose ester films ; in this respect it is similar to amyl stearate, although less stable. It is necessary to employ in conjunction with it a plasticiser such as butyl phthalate for cellulose-nitrate or benzyl alcohol for cellulose-acetate films. When used alone the maximum quantity that can be incorporated is 5% of the weight of cellulose acetate and 2% of that of the

nitrate. It is a yellow oily liquid which is not miscible with water. It does not dissolve cellulose acetate or nitrate, shellac or hard copals. It is a good solvent for ester gum, copal ester, cumarone, benzyl abietate, and is miscible with castor, linseed and other oils, also with hydrocarbons. *Characteristics :* S.G. ·87–·88. B.R. 350°–360° (decomposes). Esters 98% min.

Butyl Stearate. $CH_3(CH_2)_{16} . COO . C_4H_9$

This is a stable ester, similar to amyl stearate, useful as a lubricating and water-repelling plasticiser ; it permits a high polish and resistance to scratching to be given to cellulose ester films. The maximum permissible dose is 5% of the weight of cellulose acetate and 2% of that of cellulose nitrate. It should be used in conjunction with amyl phthalate, amyl tartrate or triacetin. M.P. 18°–20°. S.G. at 20° ·855–·860. R.I. 1·4465. B.R. 355°–368°. F.P. 145° C. (293° F.). Esters 99–100%. Acidity ·2% max. Water dissolves 0·2% at 25° C., and it dissolves 0·03% of water at 25° C. It also dissolves ester gum, copal ester, cumarone, benzyl abietate ; it is miscible with oils and hydrocarbons, but not with water. It does not dissolve cellulose esters, shellac, hard copals, or glyceryl phthalate resins. Dissolves rubber on heating.

Amyl Stearate. $CH_3(CH_2)_{16} . COO . C_5H_{11}$

This is a plasticiser of doubtful utility when used alone ; it is best employed in conjunction with another plasticiser such as triacetin or amyl phthalate. Its value lies in its water-repelling action, and it allows a high polish to be given to films, 1% of the weight of the total solids being sufficient to impart these properties to films, the maximum proportion being 2% for cellulose nitrate and 5% for cellulose acetate. It is also valuable in lacquers incorporating copal esters, for which it is an effective plasticiser. *Characteristics :* S.G. ·860–·885. B.P. about 360° C. M.P. 14° approx. R.I. 1·44–1·45. Esters 98% min., acidity ·2% max.

It is a solvent for copal ester, cumarone, benzyl abietate ; it partly dissolves ester gum, shellac and mastic, but not cellulose acetate or nitrate or vinyl acetate. It is miscible with castor, linseed and other varnish oils and with hydrocarbons, but not with water.

Cyclohexanyl Stearate

This material is an odourless white wax having M.P. 25° C. S.G. ·885. Esters 98%. Acidity ·08% max. It is insoluble in water, is stable to light and miscible with organic solvents and oils with the exception of methylated spirit.

Amyl Benzoate. $C_6H_5 . COO . C_5H_{11}$

This ester is occasionally employed as a plasticiser; it is a colourless liquid having a mild odour. S.G. ·994–1·01. R.I. 1·4945. B.P. 262°. Cub. exp. ·000858.

Amyl benzoate is a good solvent for ester gum, colophony, copal ester, cumarone, benzyl abietate, and is miscible with castor, linseed and other oils, also with hydrocarbons, but not with water. It is a poor solvent for cellulose nitrate and acetate, shellac, and hard copals, and does not dissolve glyceryl phthalate resins.

It is possible to simulate the effect of a white pigment in a cellulose acetate film by adding proportions in excess of 5% in the absence of another plasticiser.

Butyl Benzoate. $C_6H_5 . COO . C_4H_9$

This is similar to amyl benzoate in properties; it has S.G. 1·009–1·010. R.I. 1·498. Esters 98% min.

Benzyl Benzoate. $C_6H_5 . COO . CH_2 . C_6G_5$

This is a very stable ester; it can be used in proportions up to 100% and 66% by weight of cellulose nitrate and acetate respectively. It yields strong hard films. It dissolves ester gum, colophony, copal ester, congo, kauri, Sierra Leone copals, mastic, dammar, cumarone, benzyl abietate, polystyrol, methyl methacrylate resin and, on heating, hard copals. It has moderate solvent properties for shellac and glyceryl phthalate resins. It is miscible with castor and oils generally and with hydrocarbons, but not with water or glycerine. It is particularly of use when it is desired to incorporate a hard copal in a cellulose lacquer. *Characteristics:* S.G. 1·120–1·216. B.R. 323°–324°. R.I. 1·568–1·569. M.P. 16°–18° C. F.P. 298° F. (148° C.) Vis. 10. Cub. ex. ·00075. Soluble in 2 volumes of industrial alcohol at 20°.

Butylene Glycol di-Benzoate

$CH_3 . CH(OOCC_6H_5) . CH_2 . CH_2 . OOC . C_6H_5$

This plasticiser is an odourless, colourless light and water-stable liquid which imparts remarkable adhesive properties

and high gloss to cellulose nitrate. S.G. ·1·14. R.I. 1·54–1·56. Esters 98–100. Acidity ·2%.

In proportions up to 75% on cellulose nitrate and 30% on cellulose acetate; it yields clear, hard, flexible films and is a plasticiser for polylvinyl acetals.

Amyl Borate. $(C_5H_{11})_3 . BO_4$

This is a high-boiling solvent used for the purpose of imparting high adhesivity between cellulose films and metallic surfaces. Amyl borate readily liberates boric acid in contact with moisture; this acid, being a weak one, slightly attacks the metal, but without causing visible corrosion.

Amyl borate is not a solvent for cellulose esters, or only slightly so, and can therefore only be employed in limited proportions, *e.g.*, up to 10% of the total solids. It tends to reduce the inflammability of cellulose nitrate films. It can with advantage replace the boric acid used occasionally in lacquers, and is useful for preventing the gelling to cellulose nitrate-bronze powder mixtures.

Amyl borate is a solvent for ester gun, cumarone, benzyl abietate, mastic, castor, linseed and other oils. It partly dissolves copal ester and shellac. It is miscible with hydrocarbons and all the usual lacquer solvents. It does not dissolve copals or glyceryl phthalate resins. *Characteristics:* S.G. about ·865. B.R. 250°–260°. R.I. 1·42.

Di-methyl Phthalate. $C_6H_4 . (COO . CH_3)_2$

An ester which is frequently used, it is similar to di-ethyl phthalate in properties, being a colourless, light fast odourless liquid. S.G. 1·193–1·197. B.R. 282°–285°. R.I. 1·515–1·517. I.P. 132° C. F.P. 130° C. Vis. 17. Dil. rat. toluene 1·9. Water dissolves ·3%. Dissolves 1·5% of water. Di-methyl phthalate yields excellent films having good adhesion with both cellulose acetate and nitrate in proportions up to 75% of the weight of the cellulose ester. It is particularly stable to light. It is not miscible with petroleum naphtha. It plasticises rubber and polyvinyl acetals.

Di-ethyl Phthalate. $C_6H_4(COO . C_2H_5)_2$

A stable ester enjoying a wide popularity for lacquer work. It is a good plasticiser for cellulose nitrate, cellulose acetate, ethyl cellulose, di-benzyl cellulose and glyceryl phthalate

resins, but is inferior to butyl or amyl phthalate for the nitrate. It can be used to plasticise cellulose acetate in proportions up to 100% by weight of the cellulose acetate and yields strong elastic resplendent films stable to light. The maximum proportion for cellulose nitrate is 80%, and for glyceryl phthalate resin 25%.

It is a good solvent for cellulose nitrate, acetate and aceto-nitrate, ethyl cellulose, ester gum, colophony, cumarone, benzyl abietate, linoxyn, rubber chloride, glyceryl phthalate resin, vinyl resins and cyclohexanone-formaldehyde resin ; a moderate one for copal ester, shellac and mastic. Hard copals can be dissolved in it on prolonged heating. It is miscible with castor, linseed and other oils and with benzene hydrocarbons ; partly miscible with petroleums and non-miscible with water.

British Standard Specification 574—1934.[1] S.G. 1·114–1·129 (1·111–1·126 at 20°). R.I. 1·4805–1·506. Esters 98% min. Acidity ·025% max. Ash ·02% max. The material has B.P. about 295° and dissolves ·6% of water at 18° C. Water dissolves ·15%. Vis. 10 at 25°. Dil. rat. benzene 5·0, butanol 3·0, toluene 3·0. Cub. exp. ·00085. F.P. 140° C. (284° F.).

Di-ethyl phthalate is a good wetting medium in which to grind solid pigments.

Di-butyl Phthalate. $C_6H_4 . (COO . C_4H_9)_2$

This is a plasticiser which enjoys great popularity in America ; it is made by the direct action of butyl alcohol on phthalic anhydride.

It is a very stable substance and has proved to be a highly satisfactory plasticiser in actual use with cellulose nitrate, polystyrene, polyvinyl and methacrylate resins, rubber chloride and ester gums, although it is perhaps somewhat inferior to di-amyl phthalate. It does not wet pigments easily.

It is a solvent for cellulose nitrate, di-benzyl cellulose, vinyl resin, ester gum, copal ester, colophony, cumarone, benzyl abietate, mastic. It partly dissolves shellac, glyceryl phthalate resins and rubber. It dissolves hard copals and cellulose acetate on prolonged heating. It is miscible with castor, linseed and other oils and with hydrocarbons, but not with water. It can be used in quantities up to 100% of the weight of cellulose nitrate, but with cellulose acetate the maximum

quantity permissible is less than 10%. In limited proportions it is a good plasticiser for glyceryl phthalate resins.

British Standard Specification 573—1934.[1] S.G. 1·048–1·055 (1·045–1·052 at 20°). R.I. 1·492–1·495. Esters 98–100%. Acidity ·025% max. Ash ·02% max. Dibutyl phthalate has B.P. about 325°. F.P. 329° F. (164° C.). It dissolves 0·3% of water at 25° and water dissolves 0·04% at 25°. Dil. rat. benzene 4·0, toluene 2·8, butanol 20. Vis. 7_0, 5_{05}, 3_{810}, 3_{015} 2_{520}, 2_{025}.

Air Ministry Specification D.T.D.—1936. S.G. 1·049–1·056. R.I. at 15°, 1·491–1·495. Esters 95% min. Acidity 0·1% max. Ash 0·02% max.

Di-iso-butyl Phthalate. $C_6H_4 . (COO . C_4H_9)_2$

A liquid resembling di-butyl phthalate but having a slightly higher solvent power. S.G. 1·049. B.R. 305°–315°. F.P. 160°.

Di-amyl Phthalate. $C_6H_4 . (COO . C_5H_{11})_2$

Di-amyl phthalate is a substance with a very high boiling-point and of great stability, and it yields stable, elastic, weatherproof films of high tensile strength with cellulose nitrate. Di-amyl phthalate can be used in widely varying proportions; the quantity may vary up to 100% of the total solids in a cellulose nitrate lacquer, but for cellulose acetate the maximum proportions is 10%. *Characteristics:* S.G. 1·025–1·027. B.R. 336°—342°. R.I. 1·488. Esters 99–100%. Acidity ·025% max. Dil. rat. benzene 3·0, toluene 2·3, butanol 20. F.P. 180° C. It is practically odourless. Water dissolves ·01% at 25°. Dissolves ·7% of water at 25°.

It is a good solvent for ester gum, copal ester, vinyl resins, cumarone, benzyl abietate and mastic. Hard copals can be dissolved on prolonged heating. It has a limited solvent action on glyceryl phthalate resin and shellac. It is miscible with castor, linseed and other varnish oils and with hydrocarbons.

Di-hexyl Phthalate. $C_6H_4 . (COO . C_6H_{13})_2$

This consists mainly of the phthalate of di-ethyl ethanol (2 ethyl butanol 1). It as a remarkably stable ester withstanding high temperatures without decomposition and low temperatures without crystallisation. *Characteristics:* S.G.

1·019, $1·008_{30}$. R.I. 1·492. Vis. 78_{15}, 40_{25}. At –78° C. it is a non-crystalline viscous liquid.

It is a good plasticiser for cellulose nitrate in proportions up to 100%, for cellulose acetate up to 15%, and methyl methacrylate resin.

Di Lauryl Phthalate. $C_6H_4[COO . (CH_2)_{11} . CH_3]_2$

Di lauryl phthalate is the phthalate of the higher saturated aliphatic alcohol, n-dodecanol sometimes termed C_{12} alcohol. It is a neutral pale yellow almost odourless liquid of very high boiling-point, having S.G. ·9459 (9433 at 20/4°), R.I. 1·482. It imparts resistance against the prolonged action of light and moderate heat on cellulose nitrate films ; in proportions up to 66% it is a good plasticiser for cellulose acetate and nitrate.

Di-methyl-glycol Phthalate $(CH_3O.CH_2.CH_2.OC)_2.C_6H_4$

Known also as ethylene glycol mono methyl ether phthalate and as methyl cellosolve phthalate is a plasticiser for both cellulose acetate and nitrate in proportions up to 50% of the weight of the cellulose ester. It is a liquid, having S.G. 1·17 at 20°. R.I. 1·503. F.P. 174° C. (345° F.). Dissolves 3·4% of water at 20°. Water dissolves ·9% at 25°. Gasoline dissolves 2% at 20°.

Di-ethyl-glycol Phthalate. $(C_2H_5O.CH_2.CH_2.OOC)_2.C_6H_4$

This substance is the phthalic ester of ethylene glycol mono-ethyl ether, known also as di-ethoxy-ethyl phthalate and as cellosolve phthalate ; it is an excellent softener for cellulose nitrate, and it gelatinises cellulose acetate in proportions up to 50%. It is a colourless crystalline solid. M.P. 34°. S.G. 1·123. B.P. 345°. F.P. 143° C. Soluble in alcohol, acetone, benzene, insoluble in petroleum hydrocarbons. It tends to cause the darkening of cellulose nitrate films. Known industrially as " Cellosolve Phthalate."

Di-butyl Glycol Phthalate $(C_4H_9O.CH_2.CH_2.OOC)_2.C_6H_4$

Ethylene glycol mono-butyl ether phthalate is a liquid which boils at 370° with slight decomposition and possessing plasticising properties superior to either of the above. It is of special value for cellulose acetate and can be used in proportions up to 33% of the cellulose acetate. It is insoluble in water, but soluble in practically all organic solvents.

Di-phenyl Phthalate. $C_6H_4 . (COO . C_6H_5)_2$

A white odourless solid. M.P. 69°. S.G. 1·28 at 25°. Insoluble in water, slightly soluble in paraffin hydrocarbons, soluble in many other solvents. Discolours in light. Its maximum compatibility with cellulose nitrate is 80%, with acetate 50%, with gum dammar 30% ; it is also compatible with benzyl cellulose and polystyrene.

Di-ethyl Oxalate. $C_2H_5 . OOC . COO . C_2H_5$

Although possessing quite considerable solvent powers, this ester is not to be recommended for use as a lacquer solvent, since it is somewhat unstable in the presence of moisture, liberating oxalic acid and ethyl hydrogen oxalate. Technical di-ethyl oxalate has S.G. 1·084–1·087. B.R. 181°–187°. Esters 99% min. Acidity ·05%. The pure ester has S.G. 1·084. B.P. 185°. M.P. -40° F.P. 168° F. (76° C.). L.H. 69. S.H. ·43. Vis. 1·76 at 25°. Cub. exp. ·001. Dielec. const. 8. Elec. cond. 7×10^{-1}. Dissolves ·5% of water at 25°.

It is a solvent for cellulose acetate and nitrate, for ester gum and benzyl abietate ; it partly dissolves shellac, but does not dissolve copal ester or glyceryl phthalate resins.

Di-butyl Oxalate. $C_4H_9 . OOC . COO . C_4H_9$

This is a plasticising solvent for cellulose nitrate, but is not of a very permanent character, a defect common to most oxalic esters. It is a good solvent for cellulose nitrate, ester gum, copal ester, mastic, cumarone, benzyl abietate, glyceryl phthalate and vinyl acetate resin, but does not dissolve cellulose acetate or hard copals. It is miscible with castor, linseed and other oils and with hydrocarbons, but not with water. *Characteristics :* S.G. ·900–·995. B.P. 245° (pure). R.I. 1·42–1·43. Esters 99–100%. F.P. 212° F. (100° C.). S.H. ·44. Cub. exp. ·001. Dil. rat. toluene 2·6, benzene 2·4.

Di-amyl Oxalate. $C_5H_{11} . OOC . COO . C_5H_{11}$

Di-amyl oxalate is a plasticiser which is not widely used and about which little information exists. It has only a moderate solvent action for cellulose nitrate, copal ester, glyceryl phthalate resin and shellac. It does not dissolve cellulose acetate or hard copals, but is a good solvent for ester gum, cumarone, benzyl abietate and mastic. It is

miscible with castor and linseed oils and with hydrocarbons, but not with water.

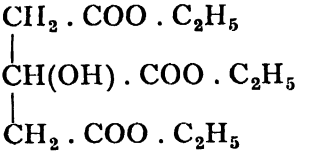
It is rather prone to hydrolysis by moisture, forming acid amyl oxalate.

Di-amyl oxalate has S.G. ·97 and B.P. about 265°. F.P. 240° F. (116° C.). It is a nearly colourless, odourless, oily liquid.

Butylene Glycol Oxalate

This is a very viscous pale yellow liquid which yields clear hard films with both cellulose acetate and nitrate in proportions up to 75%. It is insoluble in water but soluble in most organic solvents.

Tri-ethyl Citrate.



This is a plasticiser recently introduced for both cellulose acetate and nitrate, with which it can be used in proportions up to 100% by weight of the cellulose ester. The pure ester has B.P. 294°. S.G. 1·13–1·14 at 20°. R.I. 1·445. Dil. rat. benzene 9·0, toluene 3·9, xylene 2·0, butanol 4·0. It is a colourless, odourless mobile liquid having a very bitter taste. It dissolves ester gum, dammar, glyceryl phthalate resin and some albertols. It sometimes causes cellulose acetate to become coloured.

Tri-butyl Citrate

A liquid plasticiser having a weak, fruity odour. It plasticises both cellulose nitrate and acetate, the maximum permissible proportions being 75% and 20% respectively. S.G. 1·046–1·047. R.I. 1·446. Dil rat. benzene 6·8, toluene 4·9, butanol 19·0. It may contain small proportions of the dibutyl ester of acetone dicarboxylic acid. When used in excessive proportions with cellulose acetate it tends to cause lack of adhesion.

Tri-amyl Citrate

This is similar in character to tri-butyl citrate; it has S.G. 1·013. R.I. 1·447. Esters 97–100%. Acidity ·1% max. Dil. rat. benzene 5, xylene 6, butanol 11. It is a good solvent

for cellulose nitrate, ester gum, glyptals, dammar, shellac, soluble bakelites, but not for cellulose acetate.

Di-butyl Tartrate.

$$\begin{array}{l} CH(OH) \cdot COO \cdot C_4H_9 \\ | \\ CH(OH) \cdot COO \cdot C_4H_9 \end{array}$$

Butyl tartrate, like amyl tartrate, is particularly suitable for use with cellulose acetate, ethyl cellulose and glyceryl phthalate resins, being employed in quantities up to 100% of the weight of these, and up to 150% with cellulose nitrate. It yields stable weatherproof films. *Characteristics :* S.G. 1·090–1·095. B.R. 292°–312°. R.I. about 1·442. F.P. about 320° F. (160° C.). Esters 98–100%. Acidity 0·1% max. M.P. (pure) 21·8°. Dissolves 4% of water at 25° C. and 3% at 180° C. Water dissolves 1% at 25° C. Dil. rat. (cellulose nitrate) : benzene 13·5, toluene 10·7, butanol 20 ; (cellulose acetate), benzene 1·2, ethyl alcohol 1·0, butanol 0·2.

It is a good solvent for cellulose nitrate and acetate, colophony, ester gum, copal ester, benzyl abietate, sulphur, vinyl resins, glyceryl phthalate resin, methyl methacrylate resin, shellac, cumarone, and—in conjunction with benzene and methyl acetate—for ethyl cellulose. It is miscible with oils and hydrocarbons. It can be used with bakelite resins and rubber chloride.

Di-amyl Tartrate.

$$\begin{array}{l} CH(OH) \cdot COO \cdot C_5H_{11} \\ | \\ CH(OH) \cdot COO \cdot C_5H_{11} \end{array}$$

This is an exceptionally good plasticising solvent for cellulose acetate and for glyceryl phthalate resin. It enables these two substances to be effectively combined so as to give resplendent, stable, weatherproof films ; the maximum proportion recommended is 80% of the weight of the cellulose acetate. The maximum dose for cellulose nitrate is 100%.

It is manufactured by the direct esterification of tartaric acid with isoamyl alcohol and is a mixture of isomers. *Physical Characteristics :* S.G. 1·05–1·06. R.I. 1·45. B.P. about 400° C. Esters 98% min. Acidity ·1% max. Dil. rat. toluene 9·8.

It is a good solvent for cellulose nitrate and acetate, colophony, ester gum, bakelite resin, glyceryl phthalate resin, cumarone, benzyl abietate, shellac, rubber chloride and vinyl resin.

It has moderate solvent powers for copal ester, mastic, soft copals, and will not dissolve hard copals. It is miscible with castor and linseed oils and hydrocarbons ; non-miscible with water. In conjunction with benzene and methyl acetate it dissolves ethyl cellulose.

Methyl-cyclohexanyl Oxalate. $(COO . C_6H_{10} . CH_3)_2$

Methyl-cyclohexanyl oxalate is a plasticiser known industrially as " Barkite." [3] It is a viscous, practically colourless and odourless liquid consisting of a mixture of three isomerides. S.G. 1·035. Esters 98–100%. Acidity ·02% max. Insoluble in water. Anhydrous. Miscible in all proportions with the usual lacquer solvents and diluents.

It is a stable substance and is a solvent for cellulose nitrate, ethers and resins ; it has good wetting power for pigments.

The maximum proportions for plasticising cellulose acetate and nitrate are 66% and 150% respectively.

The homologous *cyclohexanyl oxalate* is a white crystalline solid, M.P. 40° C., having a faint odour. It forms a solid solution with cellulose nitrate and is compatible with resins.

Di-methyl Cyclohexanyl Oxalate. $(COO . C_6H_9 . (CH_3)_2)_2$

Known industrially as Barkite B.,[1] is a substance similar to methyl cyclohexanyl oxalate and has S.G. 1·014. Esters 98% min. Acidity ·02% max. F.P. 293° F. (147° C.).

Methyl cyclohexanyl lactate has S.G. 1·02. B.R. 230°–244°. F.P. 208° F. Esters 96%.

Methyl-cyclohexanyl Adipate
$(CH_2 . CH_2 . COO . C_6H_{11} . CH_3)_2$

Di-(methyl-cyclohexanyl) adipate, known industrially as " Sipalin A.O.M.," is a colourless neutral liquid of very high boiling-point. It is a stable ester and is a solvent for cellulose nitrate, resins, fats, rubber and oils, but not for cellulose acetate.

The ester is made by esterifying methyl-cyclo-hexanol (methylhexalin) with adipic acid, this acid being a product of the oxidation of cyclohexanol.

" Sipalin M.O.M." is a similar substance of slightly lower boiling-point, being di(methyl-cyclohexanyl)β-methyl adipate. Methyl adipic acid results from the oxidation of methyl cyclohexanol.

" Sipalin A.O.C." is di-cyclohexanyl adipate. The characteristics of these three substances are as follows :—

	B.P.	S.G.	F.P.	R.I.
Sipalin A.O.M. . .	225—232° C. at 12 mm.	1 011	1·469	189 C°.
Sipalin M.O.M. . .	216—224° C. „	1·009	1·468	195 C°.
Sipalin A.O.C. . .	212° C. „	1·030	—	185" C.

Butylene Glycol Mono-lactate

$CH_3 . CH(OH) . CH_2 . CH_2 . OOC . CH(OH) . CH_3$

This substance is a non-volatile pale yellow viscous liquid which, although completely soluble in water, yields clear, hard, flexible water-resisting films with both cellulose nitrate and acetate in proportions up to 85% of the weight of the cellulose ester. It has S.G. 1·09–1·10. R.I. 1·44–1·45. Miscible with nearly all solvents.

Mono-cresyl Glyceryl Ether

$CH_3 . C_6H_4 . O . CH_2 . CH(OH) . CH_2OH$

An almost odourless solid having the following characteristics : S.G. 1·124. R.I. 1·535. B.R. 310°–330°. M.P. 30°–50°. Solubility in water at 15° 1–1·5%. Dissolves 10% of water at 15°. Acetyl value 340–370. Non-hydrolysable, neutral. Miscible in all proportions with all the usual solvents excepting paraffin hydrocarbons. Plasticises benzyl cellulose and ethyl cellulose, but not cellulose acetate or nitrate. Inert to vulcanised rubber.

Di-cresyl Glyceryl Ether

$CH_3.C_6H_4.O.CH_2.CH(OH).CH_2.O.C_6H_4.CH_3$

Similar to mono-cresyl ether and has the following characteristics : S.G. 1·136. R.I. 1·549. B.R. 328°–340° Insoluble in water. Dissolves 10% of water at 15°. Acetyl value 220–260. Plasticises benzyl and ethyl cellulose. Soluble in all the usual organic solvents. Inert to vulcanised rubber.

Mono-cresyl Glyceryl Ether Di-acetate.

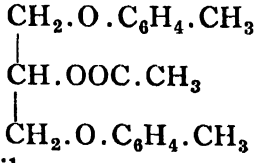
$$\begin{array}{l} CH_2.O.C_6H_4.CH_3 \\ | \\ CH.OOC.CH_3 \\ | \\ CH_2.OOC.CH_3 \end{array}$$

A liquid plasticiser for cellulose acetate, cellulose nitrate, ethyl cellulose and benzyl cellulose. This substance is much more resistant to hydrolysis than triacetin, and when used in

proportions of from 25–50% of the weight of the cellulose ester or ether, it yields non-oxidising flexible and permanent films ; the maximum permissible dose is 100%. It dissolves ester gum and is soluble in all the usual solvents and diluents.

Characteristics : B.P. about 310°. S.G. about 1·35. R.I. about 1·49.

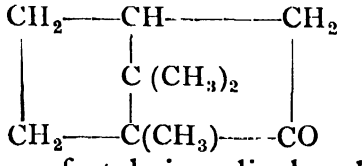
Di-cresyl Glyceryl Ether Mono-acetate.



This substance has properties similar to monocresyl glyceryl ether diacetate, but is still more resistant to hydrolysis and has a higher boiling-point.

Characteristics : B.P. about 360°. S.G. about 1·115. R.I. about 1·53.

Camphor.



The doyen of plasticisers, fast being displaced by more suitable substances, but still very largely used for celluloid. Camphor by itself has no apparent action on cellulose nitrate, but in the presence of quite small proportions of methyl, ethyl, butyl or amyl alcohols, its solvent action is rapid. It stabilises cellulose nitrate and reduces the explosibility but not the inflammability of this substance. It is useless with cellulose acetate.

As a plasticiser, it has three serious defects ; its strong odour, its relatively high vapour pressure which leads to impermanence, while excessive proportions of it tend to cause wax-like films. *Characteristics :* S.G. ·990–·995. M.P. 175°–176·6°, (pure) 178·7°. B.P. 204° sublimes. F.P. 70° C. (158° F.). L.H. 93. One part of camphor is soluble in 700 of water, or in 0·7 parts of 95% alcohol at 15° C. It readily dissolves in most organic solvents.

It is mainly produced by physical methods from Japanese camphor oil, but smaller quantities are produced by chemical synthetical methods from turpentine and other essential oils, the chief difference between the natural and synthetic products being in the optical rotation, which for natural camphor is about + 44°.

Castor Oil

Castor oil is expressed from the seeds of Ricinus communis, and consists mainly of the glycerine esters of the following acids in approximately the proportions given : ricinoleic 80%, oleic 9%, stearic 3% and linoleic 3%. The characteristics of normal oils are :—

The *British Standard Specification No.* 650—1936 [1] requires : S.G. ·958–·969 ; R.I. 1·477–1·481. Wijs iodine value 82–90 ; sap. value 177–187. Acidity 2% max. as oleic acid, acetyl value 144 min. Sol. in 4 vols. 87% alcohol at 0° C. Castor oil is soluble in most organic solvents with the exception of methyl alcohol, triacetin, diacetin and some paraffin hydrocarbons.

Castor oil is only soluble in cellulose nitrate in very limited proportions ; with most forms of cellulose nitrate, and in the absence of other substances, it gives clear films with proportions up to about 5%. Larger quantities give rise to films in which the oil is dispersed in microscopic particles, in which state it exerts a gelatinising lubricating effect. In proportions over about 25%, the microscopic particles of oil coalesce and exude, giving rise to greasiness ; by the simultaneous use of other plasticisers the greasiness may be diminished. The admixture of an equal part of tricresyl phosphate gives good results. Castor oil has a tendency to oxidise and develop rancidity. It is a solvent for ester gum and colophony. Ethyl and benzyl cellulose can be plasticised with castor oil.

Acetylated castor oil has also been used as a plasticiser, but without pronounced success.

Blown castor oil is occasionally used as a plasticiser ; its characteristics vary according to the conditions of manufacture ; in general they are S.G. about ·98. Acetyl value 150–165. Iodine number 70. Saponification value 180–190. The more prolonged the blowing the higher are the figures with the exception of the iodine number, which falls.

Butyl Acetyl Ricinoleate

This plasticiser has been recommended as a substitute for castor oil. It is a non-volatile light-coloured oil having a mild odour of castor oil ; it has a limited plasticising action on cellulose nitrate but none for cellulose acetate ; it can be used in quantities up to 100% with the nitrate before causing synæresis (sweating). *Characteristics :* S.G. at 20° ·92–·94.

R.I. 1·456–1·458. F.P. 110° C. (230° F.). B.P. about 400° C. Esters 95% min. Acid value up to 3. Dissolves about 2% of water at 25° C. It is a solvent for ester gum, manila, crepe rubber, resin ether. It partly dissolves rosin, cumarone, mastic, dammar but not shellac, sandarac, arabic or vinyls.

Ethyl Acetyl Ricinoleate

This ester has properties and uses similar to those of butyl acetyl ricinoleate. *Characteristics :* S.G. ·930–·933. R.I. 1·455–1·457. B.P. about 400°. Esters 93% min.

Benzyl Abietate. $C_{19}H_{29} . COO . CH_2 . C_6H_5$

Known also as benzyl resinate and as " Resin Ether " [5]; is a neutral semi-solid resinous plasticiser similar in appearance to Canada balsam. It is soluble in all the usual solvents. S.G. about 1·04. R.I. about 1·55. It is practically non-volatile and is a very stable ester. It can replace both resin and plasticiser and is useful for plasticising ester gum, bakelite resin and copal ester or for obtaining a soft but non-sticky film of cellulose nitrate or acetate, the addition of a small proportion of triacetin being sometimes of advantage with the two last mentioned. It is recommended for leather cloth, and for imparting adhesion, good weathering properties and gloss to cellulose nitrate films.

Ethyl Abietate. $C_{19}H_{29} . COO . C_2H_5$

This is a light amber-coloured viscous liquid. S.G. 1·03. Optical rotation about –6°. R.I. 1·52–1·53. F.P. 178° C. I.P. 216° C. (open test). M.P. –34° approx. B.P. about 350°. Soluble in all the usual anhydrous solvents. Dissolves dammar, mastic, ester gum. Insoluble in water.

Oxidises very slowly to a hard brittle resin, and tends to darken in colour. It is best used in conjunction with other plasticisers ; it blends well with castor oil.

Methyl Abietate. $C_{19}H_{29} . COO . CH_3$

A pale yellow liquid resin having latent solvent properties for cellulose nitrate developed by admixture with alcohols. It is a solvent for dammar, mastic, elemi, colophony, ester gum, and many synthetic resins ; it has some solvent action on rubber, manila, sandarac, pontianac and kauri. It is miscible with all organic solvents and immiscible with water. Methyl

abietate yields soft films with nitrocellulose, which harden on prolonged exposure due to slow oxidation. It imparts body, gloss and adhesion and resists the action of water. *Characteristics :* S.G. at 20° 1·033–1·043. R.I. 1·525–1·535. It plasticises urea-formaldehyde, ethyl cellulose, vinyl acetals, chlorinated rubber (1·015–1·025 at 25°). Acidity about 5% as abietic acid. Esters about 95% as methyl abietate. F.B. 180° C.

p-Toluene Sulphonamide. $p\text{-}CH_3.C_6H_4.SO_2.NH_2$

Known also as *p*-toluene sulphamide. It is a white odourless solid M.P. 136–7°, soluble in acetone, ethyl butyl and amyl alcohols, and their acetates, glycol ethers, benzene and most organic solvents with the exception of paraffin hydrocarbons. Alcohol dissolves 7·5% at 5°. Water dissolves 20% at 9°. Various other sulphamides have been proposed for use as plasticisers, such as the mono- and di-methyl and ethyl sulphonamides of benzene, toluene and xylene,[4] and mixtures, some of which are liquids. *Methyl p-toluene sulphamide*, M.P. 78°, has properties similar to *p*-toluene sulphamide. Both substances plasticise cellulose acetate, shellac and vinyl resins.

p-Toluene Sulphanilide. $p\text{-}CH_3.C_6H_4.SO_2.C_6H_4.NH_2$

A white crystalline solid M.P. 103°, easily soluble in acetone, alcohol, benzene, ethyl acetate and most organic solvents. It can be used to soften cellulose acetate in proportions up to 50% by weight of the cellulose acetate ; it yields rather brittle films. *Methyl p-toluene sulphanilide* is a similar substance, M.P. 95°.

Ethyl p-Toluene Sulphonate. $p\text{-}CH_3.C_6H_4.SO_3.C_2H_5$

Is a white crystalline solid M.P. 32° which is said to be slightly toxic. It is insoluble in water, but readily breaks down into *p*-toluene sulphonic acid and alcohol. It is soluble in alcohols, ether and many organic solvents.

Cresyl p-Toluene Sulphonate. $p\text{-}CH_3.C_6H_4.SO_3C_6H_4.CH_3$

This is a brown oil having a slight odour. S.G. 1·207. F.P. 184° C. It gelatinises cellulose acetate and can be used as a plasticiser in moderate proportions. The industrial article is usually a mixture of three isomers. It is also known as tolyl *p*-toluene sulphonate.

Ethyl Acetanilide. $C_6H_5N.(C_2H_5).CO.CH_3$

Known industrially as " Mannol," has a stabilising action on cellulose nitrate, which it gelatinises in a manner similar to that of camphor. In the past it has enjoyed great popularity as a substitute for camphor, its odour being but faint. It is a white crystalline solid. S.G. 1·087. M.P. 54°. B.P. 258°. F.P. 124° C. (255° F.). Soluble in most organic solvents (70% in alcohol), and slightly in water.

Acetanilide is sometimes used for similar purposes. It is a white odourless crystalline solid. M.P. 115°. B.P. 304°. S.G. at 20° 1·20. F.P. 165° C. (329° F.).

***sym.*-Di-ethyl di-phenyl Urea.**

This substance is a stabiliser as well as a softener for cellulose nitrate. It is a white crystalline solid having a slight peppery odour. M.P. 72°–73°. B.P. 325°–330°. S.G. 1·12 at 20°. F.P. 150° C. Insoluble in water, but soluble in most organic solvents. It plasticises shellac.

Resorcinyl Di-acetate

This material is occasionally used to plasticise cellulose esters, particularly the acetate. It has S.G. 1·185–1·195. R.I. 1·502–1·513. B.P. about 278°. F.P. 145° C. Esters 97% min.

Di-benzyl Ether. $C_6H_5.CH_2.O.CH_2.C_6H_5$

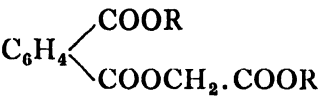
A colourless liquid having a slight almond oil odour. S.G. 1·035–1·036. B.P. 298°-300° (decomposes). F.P. 275° F. (135° C.). It is insoluble in water, but soluble in practically all organic solvents. It oxidises slowly to benzaldehyde and benzoic acid. It plasticises cellulose nitrate.

***p*-tert-Butyl Phenol.** p-$C_4H_9.C_6H_4.OH$

Like most phenols, this substance plasticises cellulose acetate. It is a white crystalline solid of somewhat pronounced odour. M.P. 98°. B.P. 236°–238°.

Another similar plasticiser of higher boiling-point is *tertiary butyl cresol.*

Alkyl Phthalyl Glycollates



These substances are similar in nature to the mixed alkyl phthalates, but contain a glycollic acid nucleus in the molecule. They are nearly colourless liquids having fruity odours, they are plasticisers for cellulose esters, polystyrol, glyptal and bakelite resins and rubber chloride.

The di-ethyl ester has S.G. 1·181 at 25°. R.I. 1·498. F.P. 190° C. Vis. 216 at 10°, 63 at 25° C.

The di-butyl ester has S.G. 1·099 at 25°. R.I. 1·489. F.P. 210° C. Vis. 137 at 10°, 51 at 25° C. Methyl phthalyl ethyl glycollate has S.G. 1·223 at 25°, R.I. 1·505. F.P. 190° C. Vis. 455 at 10°, 100 at 25° C.

Butyl Lævulinate. $CH_3 . CO . CH_2 . COO . C_4H_9$

Known also as butyl lævulate, is a colourless liquid having a mild odour resembling celery. It is a plasticiser for both cellulose acetate and nitrate, and can be used in proportions up to 100%. It is miscible with the usual organic solvents with the exception of glycols and glycerol. It dissolves 2·1% of water and water dissolves ·93%. It is a solvent for cellulose esters, ester gum, colophony, cumarone, but not for shellac, dammar or pontianac. S.G. at 20° ·9735. R.I. 1·430. B.P. about 238° C. Dil. rat. toluene 3·0.

Iso-amyl Lævulinate

This ester has properties similar to those of butyl lævulinate and has the following characteristics : S.G. at 20° ·96. R.I. 1·431. B.P. 249°. Dil. rat. toluene 3·0, butanol 7·5, gasoline 1·0.

Polyglyceryl Acetate

Known industrially as glyacol, this consists mainly of diglyceryl ether tetra acetate. It is a colourless viscous liquid similar to triacetin in character, but more viscous and possessing a higher boiling-point. B.P. about 340° C. S.G. 1·146. R.I. 1·4435. Dil. rat. toluene 0·9. It is a good plasticiser for cellulose acetate and is used in the manufacture of sheets. Maximum proportion 100%. It plasticises rubber chloride but is not miscible with vegetable oils.

Pine Oils

The term " Pine Oil " is taken to denote the natural essential oils derived from pine trees such as Pinus palustris and not containing the relatively low-boiling terpenes such as pinene, limonene, terpinene or terpinolene. They consist largely of terpineol (50–70%), to which their solvent properties are mainly due, together with borneol (5–10%), fenchyl alcohol (5–10%), camphor, menthane, anethole, methyl chavicole, cineole, dihydro terpineol and sesqui terpenes.

These oils are colourless, or nearly so, have somewhat powerful but pleasant odours and good solvent properties for cellulose nitrate, kauri, colophony, ester gum, cumarone and some albertols, glyptals and bakelites. The products which are available industrially vary considerably in characteristics ; the following figures represent the extreme limits : S.G. ·925–·945. R.I. 1·475–1·485. B.R. 180°–250°. F.P. about 170° F.

Well-known industrial products [8] of this type are Yarmor pine oil and Herco pine oil.

Vinyl Acetate

Vinyl acetate, in the polymerised form, is a solid resin which has the property of plasticising cellulose nitrate, with which it is miscible in all proportions without producing synæresis ; it is not miscible with cellulose acetate.

Polymerised vinyl acetate is available in several grades, varying in softening point from about 100° C. to 170° C., the viscosity of solutions of these several grades vary considerably with the solvent. The refractive index of all forms is about 1·47 and the specific gravity about 1·19 at 20° C. ; they are stable to heat up to 200° C., and are soluble in all the usual organic solvents with the exception of the paraffin hydrocarbons, glycols, ether and carbon disulphide.

References

1 British Standards Institution, 28 Victoria Street, S.W.1.
2 American Society for Testing Materials, 260 S. Broad Street, Philadelphia.
3 Howards & Sons Ltd., Ilford, London, E.
4 U.S. Pat. 1740854.

APPENDIX I

Trade Names and Probable Compositions

(Accuracy not Guaranteed)

Trade Name.	*Probable composition.*
Abalyn	Methyl abietate.
Abracol 203	Paratoluolsulfanilid.
Abracol 243	Di-cresyl glyceryl ether.
Abracol 777	Mono-cresyl ether diacetate.
Abracol 789	Para toluolsulfamid.
Abracol 888	Di-cresyl glyceryl ether acetate.
Abracol 1001	Tertiary butyl phenol.
Abracol 1011	Mono-cresyl glyceryl ether.
Abwaschmittel N 61	Methylacetate, ethyl propionate and methanol, mixture.
Acetonal, schwer	Higher aliphatic ketones.
Acetonal, weiss	Methylethyl ketone and lower homologues.
Aceton-Ersatz	Various low-boiling ester mixtures.
Acetin	Acetyl glycerin.
Actylol	Ethyl lactate.
Acytol	Ethyl lactate.
Adinol	Tri-ethyl citrate.
A.D.M. 100.	Linseed oil.
A.D.M. 150	Soya bean oil.
Adronol	Cyclohexanol.
Adronol acetate	Cyclohexanyl acetate.
Agfa fixator	Benzyl salicylate.
Alanol	Tetrachlorethane.
Alcoltate	Petroleum residual denaturant.
Aldehol	Petroleum residual denaturant.
Alexipon	Ethyl acetyl-salicylate.
Alkyl glycol	Mono-methyl and butyl glycol ethers.
Altal	Triphenyl phosphate.
Anol	Cyclohexanol.
Anon	Cyclohexanone.
Anozol (Anazol)	Di-ethyl phthalate.
Ansol	Ethyl alcohol and ethyl acetate.
Ansol M	Anhydrous ethyl alcohol.
Ansol ML	Ethyl alcohol 85%, ethyl acetate 6%, butanol 3% and benzol 6%.
Ansol PR	Ethyl acetate substitute containing alcohol.
Antodyne	Mono-phenyl ester.
Apco thinner	Mineral spirit.
Apex No. 1	Dibutoxyethyl phthalate.
Apex No. 2	Di-ethyleneglycol propionate.
Apex No. 3	Dibutyl ethoxy succinate.
Apex No. 4	Butyl stearate.

Apex No. 5	Lauryl butoxy ethoxy acetate.
Apex No. 6	Di-methyl ethoxy phthalate.
Arochlor	Polychlorodiphenyl.
Asordin	Carbon tetrachloride.
Avantine	*iso*-Propyl alcohol.
B2	An alkyl ricinoleate.
Banana oil	Amyl acetate.
Barkite	Methyl cyclohexanol oxalate.
Barkite B	Di-methyl cyclohexanol oxalate.
Beckolak	Benzene and ethyl alcohol.
Benzalin	Nitrobenzol.
Benzinoform	Carbon tetrachloride.
Benzolinar	Ethyl ether 1 and benzol 4.
Benzosol	Guaiacol benzoate.
Benzsuccin	Di-benzyl succinate.
Butacol	Butyl lactate.
Butanone	Methyl ethyl ketone.
Butol	Butyl butyrate.
Butoxyl	Methyl-butylene-glycol-acetate.
Butyl carbitol	Di-ethylene glycol-mono butyl ether.
Butyl cellosolve	Ethylene glycol mono butyl ether.
Butyl glykol.	Ethylene glycol mono butyl ether.
Byk special	Methyl acetate techn.
Baker's No. 1	Methyl ricinoleate.
Baker's No. 2	Ethyl ricinoleate.
Baker's P3	Butyl ricinoleate.
Baker's P4	Methyl acetyl ricinoleate.
Baker's P5	Ethyl acetyl ricinoleate.
Baker's P6	Butyl acetyl ricinoleate.
Baker's P7	Methyl undecylinate.
Baker's P8	Acetylated castor oil.
Baker's P9	Acetylated castor oil, polymerised.
Baker's P11	Methyl ester of polymerised ricinoleic acid.
Baker's P12	Ethyl ester of polymerised ricinoleic acid.
Baker's P13	Butyl ester of polymerised ricinoleic acid.
Baker's P14	P11 acetylated.
Baker's P15	P12 acetylated.
Baker's P16	P13 acetylated.
Calcitone	Acetone and methyl acetate.
Calol ethacate	Denaturant.
Camphol	Oxanilide.
Camphrosal	*p*-Toluene sulphonamide.
Canadol	Light benzine.
Carbinol	Mixture of terpenes.
Carbitol	Di-ethylene glycol mono-ethyl ether.
Casterol	Esterified castor oil.
Cecoline No. 1	Trichlorethylene.
Cecoline No. 2	Tetrachlorethylene.
Cellosolve	Ethylene glycol mono-ethyl ether.
Celludol	Toluene sulphonamide.
Cellusol	*p*-Toluene sulphonamide.

Centralite 1	Di-ethyl di-phenyl urea.
Centralite 2	Di-methyl di-phenyl urea.
Centralite 3	Methyl ethyl diphenyl urea.
Centralite 4	Ethyl phenyl ethyl *o*-toluidine urea.
Cetamoll	Mixture of phosphoric esters.
Cetamoll QU	Chlorethyl phosphate.
Chlorex	BB Dichloroethyl ether.
Chlorylen	Trichlorethylene.
Colcine	A plasticiser and partially fixed oil.
Comedol	Trichlorethylene.
Columbus spirit	Methyl alcohol.
Clophen A60	Chlorinated diphenyl.
Cresylin	Cresyl glyceryl ether
Crexylol	Toluene substitute.
Cyclohexal acetate	Cyclohexanyl acetate.
Cyclonol	A cyclohexanone-glycerine derivative.
Dec	Decahydronaphthalene.
Dekalin	Decalin, decahydronaphthaline.
Depanol	A turpentine product.
Depol	A turpentine product.
Di48	Dichlorethylene.
Di60	Dichlorethylene.
Diatol	Di-ethyl carbonate 90%.
Diacetin	Glyceryl diacetate.
Diaphanol	Methylcyclohexanyl acetate.
Diathylin	Glyceryl diacetate.
Dicresylin	Dicresyl glyceryl ether
Dieline	Dichlorethylene.
Diluols	Paraldehyde mixtures.
Diluent D	Mineral spriit.
Dional.	Ethyl acetate mixture.
Dissolvan	Methyl and ethyl acetate, alcohols and acetols.
Dissolvan CA	Low boiling ester mixture.
Dissolvan DN	Low boiling acetal mixture.
Dow P1	Di-phenyl *ter*butylphenyl phosphate.
Dow P2	Mono-phenyl di-*tert*butylphenyl phosphate.
Dow PP3	Di-phenyl *o*-chlor phenyl phosphate.
Dow P4	Mono-phenyl di-chlor phenyl phosphate.
Dow P5	Di-phenyl *o*-xylenyl phosphate.
Dow P6	Mono-phenyl di-xylenyl phosphate.
Drawin 28	Mainly ethyl acetate.
Drawin Ch	Trichlor ethylene (stabilised).
Duatol	Guaiacol acetate.
Dynalcol	1 alcohol and 1 benzol.
Elaol	Di-butyl phthalate.
Elastol	*p*-Toluene ethyl suphonamide.
E.M.A.	Methyl acetate and acetoacetic ester.
Emaillet	Tetrachlor ethane.
Enrodin	Glycol chlorhydrin mixture.
Erganol	Di-benzyl ether.
Ergol	Benzyl benzoate.

Escon	Ethyl acetyl salicylate.
Essigester	Ethyl acetate.
Ester P	Ethyl propionate.
Estergemische 13	Low-boiling ester mixture.
Esterol	Di-benzyl succinate.
Estisol.	Ethyl lactate.
Eteline	Per-chlor ethylene.
Ethox	Ethoxy ethyl phthalate.
Ethyl lactol	Petroleum fraction and alcohol.
Eufin	Di-ethyl carbonate.
Eufixin	*iso*-Amyl benzoyl glycollate.
Eusolvan	Ethyl lactate.
Exalgen	Methyl acetanilide.
Exluan	Dioxane.
Estersols	Ester mixtures of various boiling ranges.
Fermine	Di-methyl phthalate.
Ferrissol	Guaiacyl cinnamate.
Flexalyn	Diethylene glycol diabietate.
Flexalyn C	Ethylene glycol diabietate.
Flexol 3GH	Triethylene glycol dihexoate.
Flexol 3GO	Triethylene glycol dioctoate.
Formosol	Ethyl formate.
G.B. ester	Butyl glycollate.
Glyakol	Di-glyceryl ether tetra acetate.
Glycine A	Diethanol sulphide.
Glycoester	Glycolmonoacetat.
Glykosal	Glyceryl salicylate.
Grundlage	Di-methyl phthalate.
Heptalin	Methyl cyclohexanol.
Heptanaphthene	Methyl cyclohexane.
Hercolyn	Hydrogenated methyl abietate.
Hercosol 5	Pine oil derivative.
Hercosol 80	Terpene hydrocarbons and ketones.
Hexahydrokresol	Methyl cyclohexanol.
Hexalin	Cyclohexanol.
Hexalin acetate	Cyclohexanyl acetate.
Hexogen	Hexone.
Hexone	Methyl *iso*-butyl ketone.
Hexanon	Cyclohexanol.
Hydropalat A	Di-ethyl hydrophthalate.
Hydropalat B	Di-butyl hydrophthalate.
Hydroterpin	Hydrogenated turpentine product.
Hexeton	Methyl *iso*-propyl cyclohexanon.
Hexyl ketol	Ketone mixture B.R. 150°–170° C.
Hydremil	Amyl nitrite.
Hydrolinol	Methylcyclohexanol and spirit.
Hydrolin	Methyl cyclohexanol.
Industrial spirit	Ethyl alcohol.
Isopropyglykol	Ethylenglycol monoisopropylether.
Isopral	Trichlor *iso*-propyl alcohol.
Itrosyl	Ethyl nitrite.

Kalosche. . . .	Benzine.
Katarine . . .	Carbon tetrachloride.
Kelalin . . .	Decahydronaphthalene.
Kemsolene . . .	Mineral spirit.
Kessol M.A. . .	M.E.K. and anhydrous alcohol.
Ketonone B . .	Butyl benzoylbenzoate.
Ketonone E . .	Ethyl *o*-benzoylbenzoate.
Ketonone M . .	Methyl *o*-benzoylbenzoate.
Ketonone MO . .	Methoxy ethyl benzoylbenzoate.
Ketol	Ketone mixture, B.R. 60°–200° C.
Kronilyne . . .	Tri-phenyl phosphate.
Kronisol . . .	Di-butoxyethyl phthalate.
Kronitex . . .	Tri-cresyl phosphate.
Krystallol . . .	Petroleum distillate.
Lactole spirit . .	Petroleum distillate, B.R. 80°–130° C.
Lactonal . . .	Ethyl acetate.
Lak	Amyl acetate and benzol.
Lembitol . . .	Ethyl lactate.
Lewisol . .	Ester gum.
Ligroin . . .	Low-boiling petroleum.
Limonene . . .	Dipentene.
Lindol . . .	Tri-cresyl phosphate.
Losungsmittel L.C. .	Ethyl acetate substitute containing acetals.
Losungsmittel A.P.V. .	Polyglycolether product.
Losungsmittel B.P. .	Butyl propionate.
Losungsmittel C. . .	Acetal.
Losungsmittel D.A. .	Diacetone alcohol.
Losungsmittel E.13 .	Mixture of methyl acetate, ethylacetate and methanol.
Losungsmittel E.14 .	Mixture of methyl acetate, ethylacetate and methanol.
Losungsmittel E.33 .	Mixture of low-boiling esters, etc.
Losungsmittel E.M.A. .	Mixture of low-boiling esters, etc.
Losungsmittel G. . .	Glycol.
Losungsmittel G.A. .	Ethylglycol.
Losungsmittel G.A.C. .	Ethylglycol acetate.
Losungsmittel G.C. .	Glycol monoacetate.
Losungsmittel G.D. .	Glycol diacetate.
Losungsmittel G.M. .	Methylglycol.
Losungsmittel G.M.C. .	Methylglycol acetate.
Losungsmittel G.O. .	Glycol diacetate.
Losungsmittel L30 .	Terpenes.
Losungsmittel O. . .	Di-butyl oxalate.
Losungsmittel R.S. 200	Butyrolactone and valerolactone.
Losungsmittel T.A.D. .	Mixed chlorohydrocarbons.
Losungsmittel T.H.D. .	Di-chlor ethylene.
Losungsmittel L.W.H. .	Methylene dichloride.
Losungsmittel 8951 .	*iso*-Propyl alcohol.
Mannol . . .	Ethyl acetanilide.
M.C.50 . . .	Methyl alcohol, methyl acetate and ethyl acetate.
M.C.60 . . .	Methyl alcohol, methyl acetate and ethyl acetate.

M.C.75	Methyl alcohol, methyl acetate and ethyl acetate.
M.E.K.	Methyl ethyl ketone.
Metacelludol	*m*-Toluene sulphamide.
Metal	Mainly low-boiling esters.
Methylaceton	Acetone, methyl acetate, methanol.
Methlanol	Methylcyclohexanol.
Methone	Methyl acetate and acetone.
Methyl adronal	Methycyclohexanol.
Methyl adronal acetate	Methyl cyclohexanyl acetate.
Methyl anol.	Methyl cyclohexanol.
Methyl anon	Methyl cyclohexanone.
Methyl cellosolve	Ethylene-glycol mono-methyl ether.
Methyl cellosolve acetate	Ethylene-glycol mono-methyl ether acetate.
Methyl-glykol	Ethylene-glycol mono-methyl ether.
Methyglykolacetat.	Ethylene-glycol mono-methyl ether acetate.
Methyl hexalin	Methyl cyclohexanol.
Methyl hexalin acetate	Methyl cyclohexanol acetate.
Methylhexanon	Methylcyclohexanone.
Methynol	Methyl alcohol.
Mineral spirit No. 1	Petroleum distillate, B.R. 150°–215° C.
Mineral spirit No. 2	Petroleum distillate, B.R. 80°–130° C.
Mittel A.E.P.	Ethyl toluene sulphonate.
Mittel A.D.T.	Acetanilide
Mittel B.3	A sulphonamide.
Mittel B.4	A sulphonamide.
Mittel B.5	A sulphonamide.
Mittel B.6	Alkyl toluene sulphonamide.
Mittel B.7	A sulphonamide.
Mittel H.N.A.	Acetophenone.
Mittel K.P.	*p*-cresyl toluene sulphonate.
Mittel O.C.	Di-butyl oxalate.
Mittel L.30	Product from turpentine.
Mittel P.A.	Cellosolve phthalate.
Mittel P.A.	Ethyl glycol phthalate.
Mittel P.H.	Hydroxy naphthanilide.
Mittel P.I.	*p*-Toluene sulphanilide.
Mittel P.J.	Paratoluol sulphanilide.
Mittel P.M.	Di-methyl glycol phthalate.
Mittel P.O.	*p*-Toluene phenyl sulphonate.
Mittel P.11	2-3-Oxynaphtholic acid-anilide.
Mollit A	Glyceryl acetyl benzoate.
Mollit B	Glyceryl tribenzoate.
Mollit B.R. extra	Glycerine ester mixture.
Mollit I.	Di-ethyl-di phenyl urea.
Mollit II	Dimethyldiphenyl urea
Mollit IV.	Di-ethylo-tolyl urea.
Monoil	Xylene methyl-sulphonamide.
Naphthene	Cyclohexane.
Naphtol A.I.S.	Hydroxy-naphthanilide.
Natalit	3 Spirit, 2 ether
Neantin	Di-ethyl phthalate.

Neu-camphrosal	*p*-Toluene sulphamide.
Nilox ester oil	Methyl cyclohexanol oleate.
Niobe oil	Methyl benzoate.
Normanol	Ethyl lactate.
Novania	Tetrachlorethane.
Oktalin	Octohydronaphthalene.
Orthene	*o*-Dichlorbenzene.
Ozonin	Ozonised turpentine oil.
Palatinol A	Di-ethyl phthalate.
Palatinol B.B.	Benzyl butyl phthalate.
Palatinol C	Di-*n*-butyl phthalate.
Palatinol E	Di-ethyl-glycol phthalate.
Palatinol J.C.	Di-*iso*-butyl phthalate.
Palatinol M..	Di-methyl phthalate.
Palatinol O..	Di-methyl glycol phthalate.
Paracetat	*iso*-Propyl acetate.
P.C. 125	Ethyl acetate and butyl propionate.
Pentacetate	Synthetic amyl acetate.
Pentalin	Pentachlorethane.
Pentalyn	Pentaerythritol abietate.
Pentasol	Synthetic amyl alcohol.
Pentasol acetate	Synthetic amyl acetate.
Pentexel	Synthetic amyl acetate and amyl alcohol.
Peracol	Cyclohexanol and ethyl alcohol.
Peramyl alcohol	Cyclohexanol, butyl alcohol and *iso*-propyl alcohol.
Perawin	Perchlorethylene.
Permetol	Methylcyclohexanol and tetrachlorethane.
Permitol	Chlorinated diphenyl.
Petrobenzol	Mineral spirit.
Persprit	*iso*-Propyl alcohol.
Perudin	Benzyl benzoate.
Peruscabin	Benzyl benzoate.
Petrohol	*iso*-Propyl alcohol.
Phœnixine	Carbon tetrachloride.
Pinolin	Rosin spirit.
Pinradol	Pine root oil.
Placidol A	Di-amyl phthalate.
Placidol B	Di-butyl phthalate.
Placidol E	Di-ethyl phthalate.
Plassitil	Glyceryl monolactate triacetate.
Plastic A	Glyceryl tri-benzoate.
Plastic X	Tri-cresyl phosphate.
Plasticiser 64	Hexachlordiphenyl.
Plasticiser 101	Di-methyl glycol phthalate.
Plastoform I	Benzyl alcohol.
Plastoform II.	Phenyl ethyl alcohol.
Plastol A	Toluene sulphonamide.
Plastol C. II.	Mixed aromatic sulphonamides, mainly toluene sulphonamide.
Plastol M.	Alkylated toluene sulphonamide mixture.

Plastol V.G. Plastol V.B.	Ethyl toluene sulphonamide.
Plastolin I.	Benzyl abietate.
Plastolin II.	Amyl salicylate.
Plastomol P.	Toluene sulpho-anilide and toluene methyl sulphonamide.
Plastoplex	Butyl phosphate.
Polysolvan	Methyl cyclohexanone and acetate.
Prestone	Di-ethylene glycol.
Pumilin	Pine root oil.
Puran	Monochlorbenzene.
Pyranton	Spirit, acetone and diketone or cyclohexanol and cyclohexanone.
Pyranton A.	Diacetone alcohol.
Quittnerlack.	Tetrachlorethane.
R.B.A.	Butyl acetyl ricinoleate.
R.E.A.	Ethyl acetyl ricinoleate.
Remol NF	Chloralkyl phosphates.
Renol	Alcohol and carbon tetrachloride.
Resilvestrol	Synthetic balsam turpentine oil.
Resin ether	Benzyl abietate.
Ricol	Blown castor oil.
Rixolin	Petroleum and camphor oil.
Rodol N 333	Methyl alcohol and methyl acetate.
Salacetol	Ethyl acetyl salicylate.
Salicyline	Glyceryl mono-salicylate.
Salvarvol	Di-ethyl phthalate.
Sangajol	White spirit, B.P. about 160 C.
Santiciser 1	*p*-Toluene sulphonamide.
Santiciser 2	Ethyl *p*-toluene sulphonamide.
Santiciser 3	*p*-Toluene ethyl sulphonamide.
Santiciser 7	*m*-Toluene ethyl sulphonamide.
Santiciser 8	*o*- and *p*-Toluene ethyl sulphonamides.
Santiciser 9	*o*- and *p*-Toluene sulphonamides.
Santiciser 10	*o*-Cresyl *p*-toluene sulphonate.
Santiciser E15	Ethyl phthalyl ethyl glycollate.
Santiciser B.16	Butyl phthalyl butyl glycollate.
Santiciser H.	Cyclohexyl *p*-toluene sulphonamide.
Santiciser M10	*o*-*p*-*m*-Cresyl benezene sulphonate.
Santiciser M.17	Methyl phthalyl ethyl glycollate
Santiciser M.81	Methyl *o*-*p*-toluene sulphonamide.
Sepalin M.O.J.	*iso*-Propyl methyl adipate.
Sericosol	A glycol derivative.
Sextate	Methyl cyclohexanyl acetate.
Sextol.	Methyl cyclohexanol.
Sextone	Cyclohexanone.
Sextone B.	Methyl cyclohexanone.
Shellacol	Alcohol petroleum mixture.
Sinclair solvents	High naphthene paraffins.
Sipalin A.O.C.	Di-cyclo-hexanyl adipate.
Sipalin A.O.M.	Di-methyl-cyclohexanyl adipate.

Sipalin M.O.M.	Di-methyl-cyclohexanyl methyl-adipate.
Sipalin Special	Sipalin M.O.M. and a palmitic ester.
Skellysolve	Naphtha fraction.
Skellysolve P.A.	Di-ethyl glycol phthalate.
Skellysolve P.M.	Di-methyl glycol phthalate.
Skellysolve R.E.A.	Acetyl ethyl ricinoleate.
Softener 9	A tribasic alcohol.
Softener 90	Hydroxy aliphatic ester of tribasic alcohol.
Solactol	Ethyl lactate.
Solasthin	Methylene dichloride.
Solazetol	Ethyl acetyl salicylate.
Solisol	*iso*-Propyl alcohol.
Solox	100 denatured alcohol, 5 ethyl acetate and 1 gasoline.
Solvantine	Methyl *iso*-butyl carbinol.
Solvarol	Di-ethyl phthalate.
Solvarone	Di-methyl phthalate.
Solvatone	Acetone 80%, *iso*-propyl alcohol 10% and toluene 10%.
Solveol	Di-ethyl phthalate.
Solvenol No. 1	Dipentene and other terpenes from pine oil.
Solvene	Coal tar solvent naphtha, B.R. 160° 190° C.
Solvent G.C.	Ethylene glycol mono-acetate.
Solvent P.E.	Butyl acetate ex paraffins.
Solvent E33	Methyl acetate and alcohol.
Solveol	Diethyl phthalate.
Solvesso	Hydrogenated naphtha.
Solvesso 1	Toluol petroleum fraction.
Solvesso 2	Xylol petroleum fraction.
Solvohol	Glycol and polyglycol ethers.
Solvulose	Ethylene glycol mono ethyl ether.
Spasmodin	Benzyl benzoate.
Spasmin	Di-benzyl succinate.
Spectrol	Carbon tetrachloride.
Spezial-losungsmittel	Methyl acetate and methanol.
,, A.	Methyl acetate, methanol and acetone.
,, A.E. and E.F.	Mainly low-boiling esters
,, E.	Methyl acetate, ethyl acetate and methanol.
,, Hiag	Methyl acetate and methanol.
,, "Verein"	Methyl acetate acetone and methanol.
,, E.E.33	Methyl acetate, ethyl acetate and methanol.
,, E.F., E.13	Methyl acetate, ethyl acetate and methanol.
,, A.E. 14	Methyl acetate, acetone and methanol.
Spirits of wine	Ethyl alcohol.
Spiritogen	Methyl alcohol.
Spirosal	Glycol mono-salicylate.
Spritol	Methyl alcohol.
Stabilisal A.	Nitrogenous polymerisation product.
Styracol	Guaiacol cinnamate.
Sunco spirits	Petroleum fraction, B.R. 150°–215° C.
Sumatrin	Sumatra petrolbenzin.

Suresnol	Di-ethyl phthalate.
Synthin	Synthetic petroleum hydrocarbon.
Tamasol	Butyl acetate.
Tamasol J.	*iso*-Butyl acetate.
Tamasol II	Higher aliphatic alcohols with cyclic ketones.
Tamasol III.	Higher aliphatic alcohols with cyclic ketones.
Tamasol JN.	*n*-Butyl acetate.
T.C.P.	Tri-cresyl phosphate.
Tegin	Glyceryl monostearate.
Tegofan	Chlorinated rubber.
Tekol	Purified linseed stand-oil.
Terapin	Petroleum fraction.
Terlitol	Petroleum fraction.
Terpozone	Ozonised turpentine.
Tetra	Carbon tetrachloride.
Tetracol	Carbon tetrachloride.
Tetraform	Carbon tetrachloride.
Tetralex	Perchlorethylene.
Tetralin	Tetrahydro naphthalene.
Tetranap	Tetrahydro naphthalene.
Theolin	American wood turpentine.
Textile	Petroleum fraction, B.R. 65° 100° C.
T.N.P.	Tri-naphthyl phosphate.
Tolulene	Mineral spirit.
Tornext	Chlorinated rubber.
T.P.P.	Tri-phenyl phosphate.
Tri	Trichlorethylene.
Triklone	Trichlorethylene.
Tribenzoin	Glyceryl tri-benzoate.
Tributyrin	Glyceryl tributyrate.
Tricarbin	Glyceryl tricarbonate.
Trieline	Tri-chlor ethylene.
Troluoil	Petroleum fraction, B.R. 90°–130° C.
Turmintine	Petroleum fraction, B.R. 150°—215° C.
Ulol	A mixture of esters.
Utanol	Sulphurated bitumen.
Vamolin	High-boiling petroleum.
Vansol	50 Toluene and V.M.P. naphtha.
Varnolene	Petroleum fraction, B.R. 150°–210° C.
Varsol.	Mineral spirit S.G. ·782, F.P. 40° F.
V.M.P. naphtha	Mineral spirit, B.R. 100°–160° C.
Vulcanol B.	High-boiling aromatic hydrocarbons.
Westron	Tetra-chlorethane.
Westrosol	Tri-chlor ethylene.
Wood spirit	Crude methyl alcohol.
Wood naphtha	Crude methyl alcohol.
Wood alcohol	Crude methyl alcohol.
Xylidin	Nitroxylene.

APPENDIX II

Solubility Tables

THE solubilities quoted in these tables must be regarded as merely indicative and should be interpreted in the following senses :

S = Soluble to an extent deemed to be sufficient for technical purposes, the solutions obtained being such that clarification by settling, filtering or centrifuging is practicable without excessive waste.
P = Partly, moderately or difficultly soluble.
N = Not sufficiently soluble for practical purposes.
X = Soluble under certain conditions which are mentioned in the text.

There is an inevitable element of uncertainty in tables such as these on account of the variable nature of the substances under consideration. In general, it may be taken that the solubilities quoted for the natural resins refer to a good average unadulterated quality containing natural wax. The solubilities for cellulose nitrate refer to ½ sec. N.C., while those for cellulose acetate refer mainly to the B.E.S.A. 2D50 quality.

Solvents.	Cellulose nitrate.	Cellulose acetate	Ethyl cellulose.	Benzyl cellulose.	Rubber.	Rubber chloride.	Ester gum	Polystyrene	Polyvinyl acetate	Shellac.	Hard copal.	Soft manila	Hard manila	Dammar.	Kauri.	Mastic.	Sandarac.	Elemi.	Congo.	Cumarone	Colophony.	Paraffin hydrocarbon.	Vegetable oil.	Castor oil.	Methyl methacrylate.
Hydrocarbons :																									
Benzene	N	N	S	X	S	N	S	S	S	N	N	P	N	P	P	S	N	S	P	S	S	S	S	S	S
Toluene	N	N	S	X	S	S	S	S	P	N	N	P	N	P	N	S	N	S	N	S	S	S	S	S	S
Xylene	N	N		S	S	S	S	S	N	N	N	S	N	S	N	S	N	S	N	S	S	S	S	S	P
Tetrahydronaphthalene	N	N			S	S		S		N	N			S	P	S				S	S	S	S		
Decahydronaphthalene	N	N			S		S			N	N			P	N	S					S	S	S		
Dipentene (Limonene)	N	N				S	S							S	P										
Turpentine	N	N					S		N					P									N		
V.M. and P. Naphtha (Petroleum, Gasoline)	N	N																							

	Methyl alcohol	Ethyl alcohol	*n*-Propyl alcohol	*iso*-Propyl alcohol	*n*-Butyl alcohol	*iso*-Butyl alcohol	*sec*-Butyl alcohol	Amyl alcohol	Benzyl alcohol	Diacetone alcohol	Di-ethyl ether
Alcohols:											
Methyl alcohol		N	N	N	N	N	N	N	N	X	X
Ethyl alcohol	N		N	N	N	N	N	N	N	X	N
n-Propyl alcohol	N	N		N	N	N	N	N	N	X	N
iso-Propyl alcohol	N	N	N		N	N	N	N	N	X	N
n-Butyl alcohol	N	N	N	N		N	N	N	N	X	N
iso-Butyl alcohol	N	N	N	N	N		N	N	N	X	N
sec-Butyl alcohol	N	N	N	N	N	N		N	N	X	N
Amyl alcohol	N	N	N	N	N	N	N		N	X	N
Benzyl alcohol	P	P	N	N	N	N	N	N		X	N
Diacetone alcohol	S	S	S	S	S	S	S	S	S		S
Di-ethyl ether	N	N	N	N	N	N	N	N	N	X	
Ketones:											
Acetone	S	S	S	S	S	S	S	S	S	S	S
Methyl ethyl ketone	S	S	S	S	S	S	S	S	S	S	S
Methyl propyl ketone	S	S	S	S	S	S	S	S	S	S	S
Methyl amyl ketone	S	S	S	S	S	S	S	S	S	S	S
Methyl *iso*-butyl ketone	S	S	S	S	S	S	S	S	S	S	S
Butyrone, di-(*n*-propyl) ketone	P	P	P	P	P	P	P	P	P	S	P
Esters:											
Methy lacetate	S	S	S	S	S	S	S	S	S	S	S
Ethyl acetate	S	S	S	S	S	S	S	S	S	S	S
n-Propyl acetate	S	S	S	S	S	S	S	S	S	S	S
iso-Propyl acetate	S	S	S	S	S	S	S	S	S	S	S
n-Butyl acetate	S	S	S	S	S	S	S	S	S	S	S
sec-Butyl acetate	S	S	S	S	S	S	S	S	S	S	S
iso-Butyl acetate	S	S	S	S	S	S	S	S	S	S	S
Amyl acetate	S	S	S	S	S	S	S	S	S	S	S
sec-Hexyl acetate	S	S	S	S	S	S	S	S	S	S	S
n-Butyl formate	S	S	S	S	S	S	S	S	S	S	S
Amyl formate	S	S	S	S	S	S	S	S	S	S	S
Ethyl proprionate	S	S	S	S	S	S	S	S	S	S	S
n-Butyl proprionate	S	S	S	S	S	S	S	S	S	S	S
Amyl proprionate	S	S	S	S	S	S	S	S	S	S	S
Ethyl butyrate	S	S	S	S	S	S	S	S	S	S	S
n-Butyl butyrate	S	S	S	S	S	S	S	S	S	S	S
Benzyl formate	S	S	S	S	S	S	S	S	S	S	S
Benzyl acetate	S	S	S	S	S	S	S	S	S	S	S
Ethyl lactate	S	S	S	S	S	S	S	S	S	S	S
n-Butyl lactate	S	S	S	S	S	S	S	S	S	S	S
Amyl lactate	S	S	S	S	S	S	S	S	S	S	S
Butyl glycollate	S	S	S	S	S	S	S	S	S	S	S
Methyl benzoate	S	S	S	S	S	S	S	S	S	S	S
Ethyl benzoate	S	S	S	S	S	S	S	S	S	S	S
Di-ethyl carbonate	X	N	N	N	N	N	N	N	P	S	X

SOLUBILITY TABLES—*continued*

Solvents.	Cellulose nitrate.	Cellulose acetate.	Ethyl cellulose.	Benzyl cellulose.	Rubber.	Rubber chloride	Ester gum.	Polystyrene	Polyvinyl acetate	Shellac	Hard copal.	Soft manila.	Hard manila.	Dammar.	Kaun.	Mastic.	Sandarac.	Ilemi.	Congo.	Cumarone.	Colophony.	Paraffin hydrocarbon	Vegetable oil.	Castor oil.	Methyl Methacrylate
Glycols:																									
Ethylene glycol monoacetate	S	S	S		S	N	N	S	S	N	N	S	S	N	N	P	N	S	N	N	S	N	N		S
Ethylene glycol diacetate	S	S	S		S	P	P	S	S	N	N	S	S	N	N	S	N	S	N	N	S	N	N		S
Ethylene glycol mono-methyl ether	S	S	S		S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Ethylene glycol mono-ethyl ether	S	X	S		N	S	S	S	S	P	X	S	S	S	S	S	S	S	P	S	S	S	S		S
Ethylene glycol di-ethyl ether	N	N	N		N	S	S	S	S	S	N	S	S	S	S	S	S	S	S	S	S	S	S		S
Ethylene glycol mono-ethyl ether acetate	N	N	N		N	S	S	S	S	S	N	S	S	S	S	S	S	S	S	S	S	S	S		S
Ethylene glycol mono-butyl ether	S	N	N		N	S	S	S	S	S	N	S	S	S	S	S	S	S	S	S	S	S	S		S
Butylene glycol	S	S	S		S	S	S	S	S	S	S	P	S	S	S	S	S	S	P	S	S	S	S		S
Butylene glycol diacetate	S	S	S		S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Diethylene glycol	S	S	S		S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Diethylene glycol mono-acetate	S	S	S		S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Diethylene glycol mono-ethyl ether	S	S	S		S	S	P	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Dioxane	X	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Cyclohexanes:																									
Cyclohexanol	N	N	S		P	P	S	N	P	P	P	S	N	P	P	P	N	P	P	S	S	S	S		P
Cyclohexanol acetate	S	S	S		S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Methyl cyclohexanol								S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Methyl cyclohexanol acetate	S	S	S		S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Cyclohexanone	S	S	S		S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Methyl cyclohexanone	S	S	S		S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Chloro-compounds:																									
Mono-chlorhydrin	N	S	S		S	S	P	S	S	N	N	N	N	N	N	P	N	S	N	N	S	N	N		S
Di-chlorhydrin	X	S	P		S	S	S	S	S	S	P	S	S	S	S	S	S	S	S	S	S	S	S		S
Epi-chlorhydrin	S	S	S		S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S		S
Methylene dichloride	S	N	S		S	S	N	S	S	N	N	N	N	N	N	S	N	S	N	N	S	N	N		S
Chloroform	P	X	S		S	S	S	S	S	N	N	N	N	N	N	S	N	S	N	N	S	N	N		S
Carbon tetrachloride	X	N	S		S	S	S	S	S	N	N	N	N	N	N	S	N	S	N	N	S	N	N		S
Di-chlor ethane	N	X	S		S	S	S	S	S	N	N	N	N	N	N	S	N	S	N	N	S	N	N		S
Tetra-chlor ethane	S	N	S		S	S	S	S	S	N	N	N	N	N	N	S	N	S	N	N	S	N	N		S
Di-chlor ethylene	X	S	X		S	S	S	S	S	N	N	N	N	N	N	S	N	S	N	N	S	N	N		S
Tri-chlor ethylene	S	S	S		S	S	S	S	S	N	N	N	N	N	N	S	N	S	N	N	S	N	N		S
Per-chlor ethylene	S	S	S		S	S	S	S	S	N	N	N	N	N	N	S	N	S	N	N	S	N	N		S
Mono-chlor benzene	S	S	S		S	S	S	S	S	N	N	N	N	N	N	S	N	S	N	N	S	N	N		S
Di-chlor ethyl ether	S	S	S		S	S	S	S	S	N	N	N	N	N	N	S	N	S	N	N	S	N	N		S

APPENDIX III

Plasticiser proportions

Plasticiser	Percentage proportions beyond which cloudy, oily or excessively soft films result with	
	Cellulose nitrate.	Cellulose acetate
Di-Amyl phthalate	100	10
Amyl stearate	2	5
Di-Amyl tartrate	100	80
Benzyl alcohol	150	75
Benzyl benzoate	100	66
Tri-Benzyl citrate	75	20
Benzyl lævulinate	50	90
Butyl acetyl ricinoleate	100	—
Tri-Butyl citrate	75	20
Butyl lævulinate	100	100
Butyl oleate	2	5
Di-Butyl phthalate	100	10
Butyl stearate	2	5
Di-Butyl tartrate	150	100
Butylene glycol diacetate	100	100
Butylene glycol dibenzoate	75	30
Butylene glycol monolactate	85	85
Butylene glycol oxalate	75	75
Castor oil	3	—
Cresyl glyceryl diacetate	100	100
Cyclohexyl lævulinate	100	100
Tri-Ethyl citrate	100	100
Di-Ethyl-glycol phthalate	100	50
Di-Ethyl phthalate	80	100
Glyceryl tribenzoate	150	20
Glycol dilævulinate	25	60
Di-Hexyl phthalate	100	15
Di-Lauryl phthalate	66	66
Methyl cyclohexyl oxalate	150	66
Di-Methyl-glycol phthalate	50	50
Di-Methyl phthalate	75	80
Di-Phenyl phthalate	80	50
Triacetin	66	66
Trichlorphenyl phosphate	75	50
Tricresyl phosphate	100	10
Triphenyl phosphate	100	10
Vinyl acetate	∞	0

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